Thermodynamically Consistent Diffuse Interface Models for Incompressible Two-Phase Flows with Different Densities

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Abstract

A new diffuse interface model for a two-phase flow of two incompressible fluids with different densities is introduced using methods from rational continuum mechanics. The model fulfills local and global dissipation inequalities and is also generalized to situations with a soluble species. Using the method of matched asymptotic expansions we derive various sharp interface models in the limit when the interfacial thickness tends to zero. Depending on the scaling of the mobility in the diffusion equation we either derive classical sharp interface models or models where bulk or surface diffusion is possible in the limit. In the two latter cases the classical Gibbs-Thomson equation has to be modified to include kinetic terms. Finally, we show that all sharp interface models fulfill natural energy inequalities.

Key words: Two-phase flow, diffuse interface model, Cahn-Hilliard equation, free boundary value problems.
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1 Introduction

In recent years diffuse interface models have been successfully used to describe the flow of two or more immiscible fluids both for theoretical studies and numerical simulations. One fundamental advantage of these models is that they are able to describe topological transitions like droplet coalescence or droplet break-up in a natural way.

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In the case of two incompressible, viscous Newtonian fluids the basic diffuse interface model is the so-called "Model H", cf. Hohenberg and Halperin [21]. It leads to the Navier-Stokes/Cahn-Hilliard system

$$\rho \partial_t \mathbf{v} + \rho (\mathbf{v} \cdot \nabla) \mathbf{v} - \operatorname{div}(2\eta(c) D\mathbf{v}) + \nabla p = -\varepsilon \operatorname{div}(\nabla c \otimes \nabla c), \tag{1.1}$$

$$\operatorname{div} \mathbf{v} = 0, \tag{1.2}$$

$$\partial_t c + \mathbf{v} \cdot \nabla c = \operatorname{div}(m \nabla \mu), \tag{1.3}$$

$$\mu = \varepsilon^{-1} \psi'(c) - \varepsilon \Delta c. \tag{1.4}$$

Here ρ is the density, $\mathbf{v}$ is the mean velocity, $D\mathbf{v} = \frac{1}{2}(\nabla \mathbf{v} + \nabla \mathbf{v}^T)$, p is the pressure, and c is an order parameter related to the concentration of the fluids (e.g. the concentration difference or the concentration of one component). Moreover, $\eta(c) > 0$ is the viscosity of the mixture, $\varepsilon > 0$ is a (small) parameter, which is related to the "thickness" of the interfacial region, ψ is a homogeneous free energy density and μ is the chemical potential. Capillary forces due to surface tension are modeled by an extra contribution $\varepsilon \nabla c \otimes \nabla c := \varepsilon \nabla c (\nabla c)^T$ in the stress tensor leading to the term on the right-hand side of (1.1). Moreover, we note that in the modeling diffusion of the fluid components is taken into account. Therefore $\operatorname{div}(m \nabla \mu)$ is appearing in (1.3), where $m = m(c) \geq 0$ is the mobility coefficient.

One of the fundamental modelling assumptions is that the densities of both components as well as the density of the mixture ρ are constant. Of course, this restricts the applicability of the model to situations when density differences are negligible. Gurtin et al. [20] derived this model in the framework of rational continuum mechanics and showed that it satisfies the second law of thermodynamics in a mechanical version based on a local dissipation inequality.

Lowengrub and Truskinovsky [25] derived a thermodynamically consistent extension of the Model H for the case of different densities, which leads to the system:

$$\rho \partial_t \mathbf{v} + \rho (\mathbf{v} \cdot \nabla) \mathbf{v} - \operatorname{div} \mathbf{S}(c, D\mathbf{v}) + \nabla p = -\varepsilon \operatorname{div}(\rho \nabla c \otimes \nabla c), \tag{1.5}$$

$$\partial_t \rho + \operatorname{div}(\rho \mathbf{v}) = 0, \tag{1.6}$$

$$\rho \partial_t c + \rho \mathbf{v} \cdot \nabla c = \operatorname{div}(m(c) \nabla \mu), \tag{1.7}$$

$$\mu = -\rho^{-2} \frac{\partial \rho}{\partial c} p + \varepsilon^{-1} \psi'(c) - \frac{\varepsilon}{\rho} \operatorname{div}(\rho \nabla c), \tag{1.8}$$

where $\mathbf{S}(c, D\mathbf{v}) = 2\eta(c) D\mathbf{v} + \lambda(c) \operatorname{div} \mathbf{v} \, \mathbf{I}$ and $\lambda(c)$ is the bulk viscosity coefficient. Here the free energy has the density $\rho(\varepsilon^{-1} \psi(c) + \varepsilon \frac{|\nabla c|^2}{2})$ per unit volume. A simplified version of this model has been successfully used for numerical studies, cf. Lee et al. [22, 23]. In contrast, there are – to the best of the authors' knowledge – no discrete schemes available which are based on the full model (1.5)-(1.8). This may be due to fundamental new difficulties compared with Model H (1.1)-(1.4). For instance, the velocity field $\mathbf{v}$ is no longer divergence free and the pressure p enters the equation for the chemical potential (1.8). At least analytically, these difficulties could be overcome, see Abels [1] for existence of weak solutions. Mathematically

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the coupling of the Navier-Stokes (1.5)-(1.6) and the Cahn-Hilliard part (1.7)-(1.8) is much stronger and the linearized system is very different from the linearization of Model H, cf. Abels [2], where strong solutions locally in time are constructed.

Alternative generalizations of the Model H for the case of different densities were presented and discussed by Boyer [5] and Ding et al. [9]. The model by Ding et al. consists of (1.1)-(1.4), but now for a variable density $\rho = \rho(c)$. In order to justify this generalization they start from the mass balance equation

$$\partial_t \rho_j + \mathrm{div}(\rho_j \mathbf{v}_j) = 0 \tag{1.9}$$

for the individual fluids $j = 1, 2$ and define the mean velocity $\mathbf{v}$ of the mixture as *volume averaged velocity* $\mathbf{v} = u_1 \mathbf{v}_1 + u_2 \mathbf{v}_2$, where u_j is the volume fraction of fluid j. Then (1.9) yields

$$\mathrm{div}\, \mathbf{v} = 0, \tag{1.10}$$

cf. Section 2 below. In contrast to that Lowengrub and Truskinovsky define the mean velocity $\mathbf{v}$ as *mass averaged/barycentric velocity* $\rho \mathbf{v} = \rho_1 \mathbf{v}_1 + \rho_2 \mathbf{v}_2$, which yields

$$\partial_t \rho + \mathrm{div}(\rho \mathbf{v}) = 0.$$

The incompressibility relation (1.10) of course has advantages with respect to numerical simulations – see the computations related to the model by Ding et al. in [9].

Unfortunately, (1.1)-(1.4) seems to be not consistent with thermodynamics in the case when ρ is not constant. Neither global nor local energy inequalities are known to hold for (1.1)-(1.4) in that case. The model by Boyer is more complicated. But it is derived using a volume averaged mean velocity, which leads to a divergence free mean velocity field too. The further derivation of Boyer differs from the one in [9] and ours since the starting point are the equations for the conservation of linear momentum of each single fluid. Also for this model neither global nor local energy inequalities seem to be known, cf. also [4].

It is the purpose of the present paper to derive a thermodynamically consistent generalization of (1.1)-(1.4) to the case of non-matched densities based on a solenoidal velocity field $\mathbf{v}$. More precisely, we will derive the system

$$\partial_t(\rho \mathbf{v}) + \mathrm{div}(\rho \mathbf{v} \otimes \mathbf{v}) - \mathrm{div}(2\eta(\varphi)D\mathbf{v}) + \nabla p = -\hat{\sigma}\varepsilon\, \mathrm{div}(\nabla\varphi \otimes \nabla\varphi),$$
$$\mathrm{div}\, \mathbf{v} = 0,$$
$$\partial_t\varphi + \mathbf{v} \cdot \nabla\varphi = \mathrm{div}(m(\varphi)\nabla\mu_\varphi),$$

together with

$$\mu_\varphi = \hat{\sigma}\varepsilon^{-1}\psi'(\varphi) - \hat{\sigma}\varepsilon\Delta\varphi - \frac{\partial\rho}{\partial\varphi}\frac{|\mathbf{v}|^2}{2},$$

where the order parameter $\varphi = \varphi_2 - \varphi_1$ stands for the difference of volume fractions φ_j, $j = 1, 2$[1]. Here the free energy of the system has the density $\hat{\sigma}\varepsilon^{-1}f(\varphi) + \hat{\sigma}\varepsilon\frac{|\nabla\varphi|^2}{2}$

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[1]Other choices of order parameters are possible as well – see Section 2.

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(per unit volume). In comparison with the system derived in [9] there is the additional term $-\frac{\partial \rho}{\partial \varphi} \frac{|\mathbf{v}|^2}{2}$ in the equation for the chemical potential. This term vanishes in the case of matched densities, i.e., $\rho \equiv const.$. But this term is crucial in the case of non-matched densities for consistency with thermodynamics. We note that in contrast to the model by Lowengrub and Truskinovsky (1.5)-(1.8) the usual continuity equation (1.6) is not part of our system. Nevertheless there is conservation of mass in our system. More precisely, we have

$$\partial_t \rho + \operatorname{div}\left(\rho \mathbf{v} - \frac{\tilde{\rho}_2 - \tilde{\rho}_1}{2} m(\varphi) \nabla \mu\right) = 0, \tag{1.11}$$

and in Section 2 it will be shown that in fact individual masses are conserved. Note that $\tilde{\rho}_j$ is the specific density of fluid $j = 1, 2$ and that $\rho = \frac{\tilde{\rho}_1 + \tilde{\rho}_2}{2} + \frac{\tilde{\rho}_2 - \tilde{\rho}_1}{2}\varphi$. We emphasize that according to equation (1.11) the (volume averaged) velocity $\mathbf{v}$ does not describe the flux of the density. In our model the flux of the density consists of the two parts: $\rho \mathbf{v}$, describing the transport by the mean velocity, and a relative flux $-\frac{\tilde{\rho}_2 - \tilde{\rho}_1}{2} m(\varphi) \nabla \mu$ related to diffusion of the components. Hence the diffusion of the components relative to the mean velocity leads to a diffusion of the mass density in the case that $\tilde{\rho}_1 \neq \tilde{\rho}_2$. Moreover, we note that in the classical Model H effects related to diffusion of the components can play an important role and can lead to Ostwald ripening effects and disappearance of small droplets, cf. e.g. [31].

The structure of the paper is as follows: In Section 2 we will derive the generalization of Model H, described above in the framework of rational continuum mechanics. First we will use a local dissipation inequality and a choice of the energy flux as in [20] to derive restrictions for the form of the stress tensor and the chemical potential, which finally leads to our model after suitable constitutive assumptions. Then we briefly discuss the changes in the derivation if the energy flux is not specified at the beginning and Liu's Lagrange multiplier method is used, cf. [24]. In Section 3, we present a third approach to derive a thermodynamically consistent model, this time based on Onsager's variational principle. We consider the more general situation when either the system is subjected to gravitational forces or when one additional soluble species is present in both fluids. In the latter case, transport effects across the interface are taken into account, too, and we derive a diffuse interface analogue of Henry's law, cf. Section 3.

In Section 4 we discuss the sharp interface asymptotics in the limit $\varepsilon \to 0$ for the diffuse interface model together with a soluble species. This is done by using the method of formally matched asymptotics. We show that the limit system depends essentially on the choice and the scaling of the mobility. Actually, we consider four cases related to choosing the mobility degenerate or non-degenerate and letting the mobility tend to zero or not. If the mobility $m(\varphi)$ vanishes as $\varepsilon \to 0$, we end up with the classical model for a two-phase flow with the Young-Laplace law

$$-[2\eta D\mathbf{v}]_-^+ \boldsymbol{\nu} + [p]_-^+ \boldsymbol{\nu} = \sigma \kappa \boldsymbol{\nu} \qquad \text{at } \Gamma(t),$$

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where $\Gamma(t)$ is the interface between the fluids, $\boldsymbol{\nu}$ is a unit normal to $\Gamma(t)$, κ is its mean curvature, σ is a surface tension coefficient, and $[.]^+_-$ denotes the jump of a quantity at $\Gamma(t)$ in the direction of $\boldsymbol{\nu}$. Moreover, the interface is transported by the velocity of the fluid, i.e.,

$$\mathcal{V} - \boldsymbol{\nu} \cdot \mathbf{v} = 0 \qquad \text{at } \Gamma(t),$$

where $\mathcal{V}$ is the normal velocity of $\Gamma(t)$. If a soluble species with density w is present, we obtain the classical Henry condition for the jump of the concentrations of the soluble species.

In the case of a constant mobility, we obtain in the limit $\varepsilon \to 0$

$$2(\mathbf{v} \cdot \boldsymbol{\nu} - \mathcal{V}) = m_0 [\nabla \mu]^+_- \cdot \boldsymbol{\nu} \qquad \text{at } \Gamma(t),$$

for the evolution of the interface and

$$[\rho]^+_- \mathbf{v} (\mathbf{v} \cdot \boldsymbol{\nu} - \mathcal{V}) - [2\eta D\mathbf{v}]^+_- \boldsymbol{\nu} + [p]^+_- \boldsymbol{\nu} = \sigma \kappa \boldsymbol{\nu} \qquad \text{at } \Gamma(t),$$

for the jump of the stress tensor. Here μ satisfies

$$\mu = \sigma \kappa - \tfrac{1}{2} |\mathbf{v}|^2 [\rho]^+_- - [w]^+_- \qquad \text{at } \Gamma(t),$$

μ is harmonic in the bulk, and $m_0 > 0$ is a diffusion coefficient related to m. In particular the interface is no longer material and diffusion of mass through the bulk is still present in the model. In the case of a non-vanishing, degenerate mobility the evolution of the interface is governed by the surface diffusion law

$$2(\mathbf{v} \cdot \boldsymbol{\nu} - \mathcal{V}) = \hat{m} \Delta_{\Gamma(t)} \mu,$$

where $\Delta_{\Gamma(t)}$ is the Laplace-Beltrami operator of $\Gamma(t)$ and $\hat{m} > 0$ is a diffusion co-efficient related to m. In Section 5 we prove that energy estimates are valid for sufficiently smooth solutions of the sharp interface models. Finally, several important identities for the formally matched asymptotics calculations are shown in the appendix.

2   Derivation of the Model

In order to derive the diffuse interface model, one assumes a partial mixing of the macroscopically immiscible fluids in a thin interfacial region. Therefore let us intro-duce some terminology related to mixtures. In the following the fluids are labeled

by $j = 1, 2$ and they fill a domain $\Omega \subseteq \mathbb{R}^d$. The total mass density of the mixture is denoted by ρ. Moreover, ρ_j denotes the mass density of the fluid j, i.e.,

$$M_j = \int_V \rho_j(x)\, dx$$

is the mass of the fluid j contained in a set $V \subset \Omega$ and we obtain $\rho = \rho_1 + \rho_2$. Moreover, we denote by $c_j = \frac{\rho_j}{\rho}$ the *mass concentration* and note that $c_1 + c_2 = 1$.

Denoting by $\hat{\mathbf{J}}_j$ the mass flux of fluid j, the mass balance equation in local form is given by

$$\partial_t \rho_j + \operatorname{div} \hat{\mathbf{J}}_j = 0.$$

Defining the velocities $\mathbf{v}_j$, $j = 1, 2$, of the single fluids as $\mathbf{v}_j = \hat{\mathbf{J}}_j / \rho_j$ the mass balance equation can be rewritten as

$$\partial_t \rho_j + \operatorname{div}(\rho_j \mathbf{v}_j) = 0.$$

In what follows we assume that the volume occupied by a given amount of mass of the single fluids does not change after mixing, i.e., the excess volume due to mixing is zero. If $\tilde{\rho}_j$ is the specific (constant) density of the unmixed fluid j, we introduce $u_j = \frac{\rho_j}{\tilde{\rho}_j}$. The assumption that the excess volume is zero results in

$$u_1 + u_2 = 1. \tag{2.1}$$

Expressed in terms of the mass concentrations c_1 and c_2, condition (2.1) reads as

$$\frac{c_1\, \rho}{\tilde{\rho}_1} + \frac{c_2\, \rho}{\tilde{\rho}_2} = 1 \qquad \Longleftrightarrow \qquad \frac{1}{\rho} = \frac{c_1}{\tilde{\rho}_1} + \frac{c_2}{\tilde{\rho}_2}.$$

Introducing the mass concentration difference $c = c_2 - c_1$, the above relation implies that $\rho = \hat{\rho}(c)$ with a function $\hat{\rho}$ defined via

$$\frac{1}{\hat{\rho}(c)} = \frac{\frac{1}{2}(c+1)}{\tilde{\rho}_2} + \frac{\frac{1}{2}(1-c)}{\tilde{\rho}_1}.$$

We remark that possible choices for the order parameter in the phase field model are the mass concentration difference c, the density difference $\bar{\rho} := \rho_2 - \rho_1$ or the difference of volume fractions $u := u_2 - u_1$.

We now introduce a suitable averaged velocity of the mixture. In contrast to the *mass averaged/barycentric velocity* $\tilde{\mathbf{v}}$ given by $\rho\tilde{\mathbf{v}} = \rho_1\mathbf{v}_1 + \rho_2\mathbf{v}_2$, cf. Lowengrub and Truskinovsky [25], we choose the volume averaged velocity $\mathbf{v}$ of the mixture as in Boyer [5] and Ding et al. [9]. More precisely, we define

$$\mathbf{v} = u_1\mathbf{v}_1 + u_2\mathbf{v}_2 = \frac{\rho_1}{\tilde{\rho}_1}\mathbf{v}_1 + \frac{\rho_2}{\tilde{\rho}_2}\mathbf{v}_2,$$

cf. [5, 9]. As a consequence, we obtain, using the fact that the $\tilde{\rho}_j$'s are constants,

$$\operatorname{div} \mathbf{v} = \operatorname{div}(\tfrac{\rho_1}{\tilde{\rho}_1}\mathbf{v}_1) + \operatorname{div}(\tfrac{\rho_2}{\tilde{\rho}_2}\mathbf{v}_2) = \operatorname{div}(\tfrac{\hat{\mathbf{J}}_1}{\tilde{\rho}_1} + \tfrac{\hat{\mathbf{J}}_2}{\tilde{\rho}_2}) = -\partial_t \left(\tfrac{\rho_1}{\tilde{\rho}_1} + \tfrac{\rho_2}{\tilde{\rho}_2} \right) = -\partial_t 1 = 0. \quad (2.2)$$

Furthermore, we denote by $\mathbf{J}_j = \hat{\mathbf{J}}_j - \rho_j \mathbf{v}$ the mass flux of the fluid j relative to the velocity $\mathbf{v}$, i.e.,

$$\partial_t \rho_j + \operatorname{div}(\rho_j \mathbf{v}) + \operatorname{div} \mathbf{J}_j = 0.$$

Because of (2.2) and $\rho_j = \rho c_j = \tilde{\rho}_j u_j$, we have

$$\partial_t(\rho c_j) + \mathbf{v} \cdot \nabla(\rho c_j) + \operatorname{div} \mathbf{J}_j = 0$$

or equivalently,

$$\partial_t u_j + \mathbf{v} \cdot \nabla u_j + \operatorname{div} \tilde{\mathbf{J}}_j = 0,$$

where $\tilde{\mathbf{J}}_j = \tfrac{\mathbf{J}_j}{\tilde{\rho}_j}$. Because of $u_1 + u_2 = 1$, we require $\tilde{\mathbf{J}}_1 + \tilde{\mathbf{J}}_2 = \tfrac{\mathbf{J}_1}{\tilde{\rho}_1} + \tfrac{\mathbf{J}_2}{\tilde{\rho}_2} = 0$, cf. (2.2).
In particular, we obtain

$$\partial_t(\rho c) + \mathbf{v} \cdot \nabla(\rho c) + \operatorname{div} \mathbf{J} = 0, \qquad (2.3)$$

where $\mathbf{J} = \mathbf{J}_2 - \mathbf{J}_1$. In addition we have

$$\partial_t \rho = \partial_t(\rho_1 + \rho_2) = -\operatorname{div}(\mathbf{J}_1 + \rho_1 \mathbf{v} + \mathbf{J}_2 + \rho_2 \mathbf{v}) = -\operatorname{div}(\rho \mathbf{v} + \mathbf{J}_1 + \mathbf{J}_2).$$

If $\tilde{\rho}_1 \neq \tilde{\rho}_2$, we have in general $\operatorname{div}(\mathbf{J}_1 + \mathbf{J}_2) \neq 0$. Hence the classical continuity equation does not hold with respect to the velocity $\mathbf{v}$. This reflects the fact that we allow for mass diffusion in the system.

Instead of c, one could use $u := u_2 - u_1$ as order-parameter. Because of

$$\rho = \rho c_1 + \rho c_2 = \tilde{\rho}_1 u_1 + \tilde{\rho}_2 u_2, \qquad (2.4)$$
$$\rho c = \rho c_2 - \rho c_1 = \tilde{\rho}_2 u_2 - \tilde{\rho}_1 u_1 \qquad (2.5)$$

and $u_2 = \tfrac{1+u}{2}$, $u_1 = \tfrac{1-u}{2}$, we can also assume that $\rho = \hat{\rho}(u)$ and $\rho c = \widehat{\rho c}(u)$. In order to have flexibility in the choice of the order parameter, we assume that $\rho = \hat{\rho}(\varphi)$ and $\rho c = \widehat{\rho c}(\varphi)$ for some order parameter φ such that

$$\partial_t \widehat{\rho c}(\varphi) + \mathbf{v} \cdot \nabla \widehat{\rho c}(\varphi) + \operatorname{div} \mathbf{J} = 0, \qquad (2.6)$$

where $\rho c = \widehat{\rho c}(\varphi)$ is the density difference. This is equivalent to

$$\frac{\partial(\widehat{\rho c})}{\partial \varphi} \left(\partial_t \varphi + \mathbf{v} \cdot \nabla \varphi \right) = -\operatorname{div} \mathbf{J}. \qquad (2.7)$$

As in Gurtin et al. [20], we assume that the inertia and kinetic energy due to the motion of the fluid relative to the gross motion is negligible. Therefore we consider the mixture as a single fluid with velocity $\mathbf{v}$, which satisfies the laws of conservation of linear and angular momentum of continuum mechanics with respect to the volume

averaged velocity. The density and the stress tensor are assumed to depend on additional internal variables like φ and $\nabla\varphi$. I.e., we assume that

$$\partial_t(\rho\mathbf{v}) + \operatorname{div}(\rho\mathbf{v}\otimes\mathbf{v}) = \operatorname{div}\mathbf{T} \qquad (2.8)$$

for a stress tensor $\mathbf{T}$, which has to be specified by constitutive assumptions. Here external forces are neglected for simplicity.

Because of the constraint $\operatorname{div}\mathbf{v} = 0$, the stress tensor $\mathbf{T}$ is only determined up to $p\mathbf{I}$ for some scalar quantity p. Hence we make the *ansatz*

$$\mathbf{T} = \widetilde{\mathbf{S}} - p\mathbf{I} \qquad \text{where } \widetilde{\mathbf{S}} = \hat{\mathbf{S}}(D\mathbf{v}, \varphi, \nabla\varphi).$$

In order to specify the behavior of the mixture, we will make several constitutive assumptions on the form of the stress tensor $\mathbf{T}$ and the relative mass flux $\mathbf{J}$ in the following.

Finally, we assume the relative motion of the fluids to be diffusive, and we introduce a Helmholtz free energy density $f(\varphi, \nabla\varphi)$ (per unit volume). It will play the role of an interfacial energy for the diffuse interface. The total energy in a volume V is then obtained as the sum of the kinetic and the free energy, i.e.,

$$E_V(\varphi, \mathbf{v}) = \int_V \hat{\rho}(\varphi)\frac{|\mathbf{v}|^2}{2}\,dx + \int_V f(\varphi, \nabla\varphi)\,dx = \int_V e(\mathbf{v}, \varphi, \nabla\varphi)\,dx,$$

where $e(\mathbf{v}, \varphi, \nabla\varphi) := \hat{\rho}(\varphi)\frac{|\mathbf{v}|^2}{2} + f(\varphi, \nabla\varphi)$.

2.1 Derivation based on a Local Dissipation Inequality and Microstresses

In the following $V(t) \subseteq \Omega$ shall denote an arbitrary volume that is transported with the flow.

In order to describe the change of the free energy due to diffusion, we introduce a *chemical potential* μ and the outer unit normal $\boldsymbol{\nu}$ to $\partial V(t)$ such that

$$-\int_{\partial V(t)} \mu\,\mathbf{J}\cdot\boldsymbol{\nu}\,ds_x.$$

is the energy transported into $V(t)$ by diffusion and ds_x denotes integration with respect to the surface measure.

Surface forces: Moreover, we assume the existence of a generalized (vectorial) surface force $\boldsymbol{\xi}$ such that

$$\int_{\partial V(t)} \dot{\varphi}\,\boldsymbol{\xi}\cdot\boldsymbol{\nu}\,ds_x$$

represents the working due to microscopic stresses. Above and in the following $\dot{\varphi}$ is the material derivative $\partial_t\varphi + \mathbf{v}\cdot\nabla\varphi$. Finally, we note that

$$\int_{\partial V(t)} (\mathbf{T}\boldsymbol{\nu})\cdot\mathbf{v}\,ds_x$$

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describes the working in a given volume $V(t)$ due to the macroscopic stresses in the fluid.

Second law of thermodynamics/local dissipation inequality: As in [20], we assume the following dissipation inequality, which is the appropriate formulation of the second law of thermodynamics in an isothermal situation:

$$\frac{d}{dt} \int_{V(t)} e(\mathbf{v}, \varphi, \nabla\varphi) \, dx \leq \int_{\partial V(t)} (\mathbf{T}\boldsymbol{\nu}) \cdot \mathbf{v} \, ds_x + \int_{\partial V(t)} \dot{\varphi}\, \boldsymbol{\xi} \cdot \boldsymbol{\nu} \, ds_x - \int_{\partial V(t)} \mu \mathbf{J} \cdot \boldsymbol{\nu} \, ds_x$$

for every volume $V(t)$ transported with the flow. This means that the change of total energy in time is bounded by the working due to macroscopic and microscopic stresses and the change of energy due to diffusion.

We recall the transport theorem, see e.g. Liu [24, Theorem 2.1.]:

$$\frac{d}{dt} \int_{V(t)} f \, dx = \int_{V(t)} \partial_t f \, dx + \int_{\partial V(t)} \boldsymbol{\nu} \cdot \mathbf{v} f \, ds_x = \int_{V(t)} (\partial_t f + \mathrm{div}(\mathbf{v}f)) \, dx$$

where the exterior normal velocity of $V(t)$ is given by $\boldsymbol{\nu} \cdot \mathbf{v}(t)$ on $\partial V(t)$, i.e., $V(t)$ is transported with the flow described by $\mathbf{v}$. Therefore the equivalent local form is

$$\partial_t e + \mathbf{v} \cdot \nabla e - \mathrm{div}(\mathbf{T} \cdot \mathbf{v}) - \mathrm{div}(\dot{\varphi}\boldsymbol{\xi}) + \mathrm{div}(\mu\mathbf{J}) =: -\mathcal{D} \leq 0. \tag{2.9}$$

Using (1.10), (2.6) and (2.8), we will simplify $\mathcal{D}$. First of all, multiplying (2.8) with $\mathbf{v}$ and using (2.7), one easily obtains

$$\partial_t \left(\rho \frac{|\mathbf{v}|^2}{2} \right) + \mathbf{v} \cdot \nabla \left(\rho \frac{|\mathbf{v}|^2}{2} \right) = \mathrm{div}(\mathbf{T} \cdot \mathbf{v}) - \mathbf{T} : \nabla\mathbf{v} - \dot{\varphi}\frac{\partial\rho}{\partial\varphi}\frac{|\mathbf{v}|^2}{2} \tag{2.10}$$

since

$$\partial_t(\rho\mathbf{v}) \cdot \mathbf{v} + \mathrm{div}(\rho\mathbf{v} \otimes \mathbf{v}) \cdot \mathbf{v} = \partial_t \left(\rho \frac{|\mathbf{v}|^2}{2} \right) + \mathbf{v} \cdot \nabla \left(\rho \frac{|\mathbf{v}|^2}{2} \right) + (\partial_t\rho + \mathbf{v} \cdot \nabla\rho)\frac{|\mathbf{v}|^2}{2}.$$

Moreover,

$$\partial_t f + \mathbf{v} \cdot \nabla f = \frac{\partial f}{\partial\varphi}\dot{\varphi} + \frac{\partial f}{\partial\nabla\varphi} \cdot (\nabla\varphi)^{\cdot} \tag{2.11}$$

and

$$\begin{aligned}
\mathrm{div}(\dot{\varphi}\boldsymbol{\xi}) - \mathrm{div}(\mu\mathbf{J}) &= \dot{\varphi}\,\mathrm{div}\,\boldsymbol{\xi} + \nabla(\dot{\varphi}) \cdot \boldsymbol{\xi} + \mu\frac{\partial\widehat{\rho c}}{\partial\varphi}\dot{\varphi} - \nabla\mu \cdot \mathbf{J} \\
&= (\tfrac{\partial\widehat{\rho c}}{\partial\varphi}\mu + \mathrm{div}\,\boldsymbol{\xi})\dot{\varphi} + (\nabla\varphi)^{\cdot} \cdot \boldsymbol{\xi} + \nabla\mathbf{v} : (\nabla\varphi \otimes \boldsymbol{\xi}) - \nabla\mu \cdot \mathbf{J},
\end{aligned}$$

because of (2.7) and where we have used

$$\partial_{x_j}\dot{\varphi} = \partial_t\partial_{x_j}\varphi + \mathbf{v} \cdot \nabla\partial_{x_j}\varphi + \partial_{x_j}\mathbf{v} \cdot \nabla\varphi = (\partial_{x_j}\varphi)^{\cdot} + \partial_{x_j}\mathbf{v} \cdot \nabla\varphi. \tag{2.12}$$

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Thus we conclude that (2.9) is equivalent to

$$-\mathcal{D} = \left(\frac{\partial f}{\partial \varphi} - \operatorname{div} \boldsymbol{\xi} - \frac{\partial \widehat{\rho c}}{\partial \varphi} \mu - \frac{\partial \rho}{\partial \varphi} \frac{|\mathbf{v}|^2}{2} \right) \dot{\varphi}$$
$$+ \left(\frac{\partial f}{\partial \nabla \varphi} - \boldsymbol{\xi} \right) (\nabla \varphi)^{\cdot} - (\widetilde{\mathbf{S}} + \nabla \varphi \otimes \boldsymbol{\xi}) : \nabla \mathbf{v} + \nabla \mu \cdot \mathbf{J} \leq 0, \qquad (2.13)$$

where we have used $\operatorname{div} \mathbf{v} = 0$.

In order to motivate the constitutive assumptions, we will derive some restrictions for the constitutive relations specifying $\widetilde{\mathbf{S}}, \mu, \mathbf{J}, \xi$ by an argument typical for rational continuum mechanics: To this end, we assume that $\widetilde{\mathbf{S}}, \mathbf{J}, \boldsymbol{\xi}$ are functions of $D\mathbf{v}, \varphi, \nabla \varphi, \mu, \nabla \mu$ only. Moreover, we assume that $\widetilde{\mathbf{S}}$ is symmetric in order to have conservation of angular momentum. Invoking general external forces and mass supplies in the equations, one argues that $\varphi, \dot{\varphi}, \nabla \varphi, (\nabla \varphi)^{\cdot}, \mu, \nabla \mu, (\nabla \mathbf{v} - \frac{1}{3} \operatorname{div} \mathbf{v} \mathbf{I})$ can attain arbitrary values for a given point in space and time and since f and $\boldsymbol{\xi}$ do not depend on $\dot{\varphi}, (\nabla \varphi)^{\cdot}$, we conclude from (2.13) that

$$\boldsymbol{\xi} - \frac{\partial f}{\partial \nabla \varphi}(\varphi, \nabla \varphi) = 0$$

necessarily. In particular, $\boldsymbol{\xi}$ depends only on $\varphi, \nabla \varphi$. Hence (2.13) reduces to

$$-\mathcal{D} = \left(\frac{\partial f}{\partial \varphi} - \operatorname{div} \boldsymbol{\xi} - \frac{\partial \widehat{\rho c}}{\partial \varphi} \mu - \frac{\partial \rho}{\partial \varphi} \frac{|\mathbf{v}|^2}{2} \right) \dot{\varphi}$$
$$-(\widetilde{\mathbf{S}} + \nabla \varphi \otimes \boldsymbol{\xi}) : D\mathbf{v} - (\nabla \varphi \otimes \boldsymbol{\xi}) : \frac{1}{2}(\nabla \mathbf{v} - \nabla \mathbf{v}^T) + \nabla \mu \cdot \mathbf{J} \leq 0, \quad (2.14)$$

where $D\mathbf{v} = \frac{1}{2}(\nabla \mathbf{v} + \nabla \mathbf{v}^T)$. Since the skew part of $\nabla \mathbf{v}$ can attain arbitrary values independent of $D\mathbf{v}$, we conclude that

$$\boldsymbol{\xi} \otimes \nabla \varphi = \nabla \varphi \otimes \boldsymbol{\xi}.$$

Thus $|\boldsymbol{\xi}|^2 |\nabla \varphi|^2 = (\nabla \varphi \cdot \boldsymbol{\xi})^2$ and therefore

$$\boldsymbol{\xi}(\varphi, \nabla \varphi) = a(\varphi, \nabla \varphi) \nabla \varphi = \frac{\partial f}{\partial \nabla \varphi}(\varphi, \nabla \varphi) \qquad (2.15)$$

for some $a(\varphi, \nabla \varphi)$.

On the other hand, the first term after the equality sign in (2.14) is linear in $\dot{\varphi}$ and $f, \mathbf{J}$ and μ are assumed to be independent of $\dot{\varphi}$. Therefore the first term in (2.14) has to vanish to satisfy (2.14) in general and

$$\frac{\partial \widehat{\rho c}}{\partial \varphi} \mu = \frac{\partial f}{\partial \varphi} - \operatorname{div}(a(\varphi, \nabla \varphi) \nabla \varphi) - \frac{\partial \rho}{\partial \varphi} \frac{|\mathbf{v}|^2}{2}.$$

Finally, the local dissipation inequality is satisfied if and only if

$$\mathcal{D} = \left(\widetilde{\mathbf{S}} + \nabla \varphi \otimes \frac{\partial f}{\partial \nabla \varphi} \right) : D\mathbf{v} - \nabla \mu \cdot \mathbf{J} \geq 0. \qquad (2.16)$$

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Here $\widetilde{\mathbf{S}} + \nabla\varphi \otimes \frac{\partial f}{\partial\nabla\varphi}$ is also called viscous stress tensor since it corresponds to irreversible changes of the energy due to friction in the fluids.

Constitutive assumptions: Motivated by Newton's rheological law, we assume that

$$\widetilde{\mathbf{S}} + \nabla\varphi \otimes \frac{\partial f}{\partial\nabla\varphi} = 2\eta(\varphi)D\mathbf{v}$$

for some function $\eta(\varphi) \geq 0$.

Finally, we choose $\mathbf{J}(\varphi, \nabla\varphi, \mu, \nabla\mu)$ in the form

$$\mathbf{J}(\varphi, \nabla\varphi, \mu, \nabla\mu) = -\tilde{m}(\varphi)\nabla\mu,$$

where $\tilde{m}(\varphi) \geq 0$, which corresponds to a generalized Fick's law. We remark that $\mathbf{J}$ can be chosen to be nonlinear with respect to $\nabla\mu$ as long as (2.16) is fulfilled.

Summing up, we derived the following diffuse interface model:

$$\partial_t(\rho\mathbf{v}) + \operatorname{div}(\rho\mathbf{v} \otimes \mathbf{v}) - \operatorname{div}(2\eta(\varphi)D\mathbf{v}) + \nabla p = -\operatorname{div}(a(\varphi, \nabla\varphi)\nabla\varphi \otimes \nabla\varphi), \quad (2.17)$$

$$\operatorname{div}\mathbf{v} = 0, \quad (2.18)$$

$$\partial_t\widehat{\rho c}(\varphi) + \mathbf{v} \cdot \nabla\widehat{\rho c}(\varphi) = \operatorname{div}(\tilde{m}(\varphi)\nabla\mu) \quad (2.19)$$

together with

$$\frac{\partial\widehat{\rho c}}{\partial\varphi}\mu = \frac{\partial f}{\partial\varphi}(\varphi, \nabla\varphi) - \operatorname{div}(a(\varphi, \nabla\varphi)\nabla\varphi) - \frac{\partial\rho}{\partial\varphi}\frac{|\mathbf{v}|^2}{2}, \quad (2.20)$$

where $a(\varphi, \nabla\varphi)$ satisfies (2.15). Assuming the normal component of $\mathbf{v}$ and the normal derivative of μ to vanish on the boundary of the fluid domain Ω, $\int_\Omega \widehat{\rho c}(\cdot, t)\, dx$ is a constant in time. By (2.4) and (2.5), we may express both mass densities as affine linear functions of $\widehat{\rho c}$. Hence, the total mass $\int_\Omega \rho_i\, dx$, $i = 1, 2$, of each liquid component is conserved.

If $\varphi = c$ is the mass concentration difference, then $\widehat{\rho c}(c) = \hat{\rho}(c)c$, and we obtain

$$\partial_t(\rho\mathbf{v}) + \operatorname{div}(\rho\mathbf{v} \otimes \mathbf{v}) - \operatorname{div}(2\eta(c)D\mathbf{v}) + \nabla p = -\operatorname{div}(a(c, \nabla c)\nabla c \otimes \nabla c), \quad (2.21)$$

$$\operatorname{div}\mathbf{v} = 0, \quad (2.22)$$

$$\partial_t(\rho c) + \mathbf{v} \cdot \nabla(\rho c) = \operatorname{div}(\tilde{m}(c)\nabla\mu) \quad (2.23)$$

together with

$$\frac{\partial(\widehat{\rho c})}{\partial c}\mu = \frac{\partial f}{\partial c}(c, \nabla c) - \operatorname{div}(a(c, \nabla c)\nabla c) - \frac{\partial\rho}{\partial c}\frac{|\mathbf{v}|^2}{2}. \quad (2.24)$$

Here

$$\frac{\partial(\widehat{\rho c})}{\partial c} = \alpha\rho^2 \quad \text{with } \alpha = \frac{1}{2\tilde{\rho}_1} + \frac{1}{2\tilde{\rho}_2}.$$

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In the case that $\varphi = \rho c$ is the density difference, we have $\widehat{\rho c}(\varphi) = \varphi$, $\frac{\partial \widehat{\rho c}}{\partial \varphi} = 1$, and therefore

$$\partial_t(\rho \mathbf{v}) + \mathrm{div}(\rho \mathbf{v} \otimes \mathbf{v}) - \mathrm{div}\,(2\eta(\varphi)D\mathbf{v}) + \nabla p = -\,\mathrm{div}(a(\varphi, \nabla\varphi)\nabla\varphi \otimes \nabla\varphi), \quad (2.25)$$

$$\mathrm{div}\,\mathbf{v} = 0, \quad (2.26)$$

$$\partial_t\varphi + \mathbf{v} \cdot \nabla\varphi = \mathrm{div}(\tilde{m}(\varphi)\nabla\mu) \quad (2.27)$$

and

$$\mu = \frac{\partial f}{\partial \varphi}(\varphi, \nabla\varphi) - \mathrm{div}(a(\varphi, \nabla\varphi)\nabla\varphi) - \frac{\partial \rho}{\partial \varphi}\frac{|\mathbf{v}|^2}{2}. \quad (2.28)$$

Finally, in the case that $\varphi = u_2 - u_1$ is the difference of volume fractions, we have $\widehat{\rho c}(\varphi) = \frac{\tilde{\rho}_2 - \tilde{\rho}_1}{2} + \frac{\tilde{\rho}_1 + \tilde{\rho}_2}{2}\varphi$ and we obtain the system (2.25), (2.26) together with

$$\partial_t\varphi + \mathbf{v} \cdot \nabla\varphi = -\,\mathrm{div}\,\mathbf{J}_\varphi, \quad (2.29)$$

$$\mu_\varphi = \frac{\partial f}{\partial \varphi}(\varphi, \nabla\varphi) - \mathrm{div}(a(\varphi, \nabla\varphi)\nabla\varphi) - \frac{\tilde{\rho}_2 - \tilde{\rho}_1}{2}\frac{|\mathbf{v}|^2}{2} \quad (2.30)$$

where we use a rescaled flux $\mathbf{J}_\varphi = \left(\frac{\tilde{\rho}_1 + \tilde{\rho}_2}{2}\right)^{-1}\mathbf{J}$, and a rescaled chemical potential $\mu_\varphi = \frac{\tilde{\rho}_1 + \tilde{\rho}_2}{2}\mu$. We hence obtain

$$\mathbf{J}_\varphi = -m(\varphi)\nabla\mu_\varphi,$$

where $m(\varphi) = \left(\frac{\tilde{\rho}_1 + \tilde{\rho}_2}{2}\right)^{-2}\tilde{m}(\varphi)$. Usually we take the difference of volume fractions as order parameter. This has the advantage that the mass difference depends linearly on the order parameter and as usual in phase field models the values $\varphi = \pm 1$ correspond to unmixed "pure" phases.

2.2 Derivation based on a Local Dissipation Inequality and the Lagrange Multiplier Approach

It is also possible to exploit a dissipation inequality without introducing generalized surface forces. We now assume a dissipation inequality

$$\frac{d}{dt}\int_{V(t)} e(\mathbf{v}, \varphi, \nabla\varphi)\,dx + \int_{\partial V(t)} \mathbf{J}_e \cdot \boldsymbol{\nu}\,ds_x \leq 0$$

for every volume $V(t)$ transported with the flow for some general *energy flux* $\mathbf{J}_e$, which will be specified later.

Then the equivalent local form is

$$\partial_t e + \mathbf{v} \cdot \nabla e + \mathrm{div}\,\mathbf{J}_e \leq 0. \quad (2.31)$$

Because of the conservation law (2.3), we conclude that for every scalar function λ_φ the inequality

$$-\mathcal{D} := \partial_t e + \mathbf{v} \cdot \nabla e + \mathrm{div}\,\mathbf{J}_e - \lambda_\varphi\left(\partial_t(\rho c) + \mathbf{v} \cdot \nabla(\rho c) + \mathrm{div}\,\mathbf{J}\right) \leq 0 \quad (2.32)$$

has to be valid.

Using (2.8), (2.10), (2.11) we obtain that (2.32) is equivalent to

$$-\mathcal{D} = \left(\frac{\partial f}{\partial \varphi} - \frac{\partial \rho}{\partial \varphi} \frac{|\mathbf{v}|^2}{2} - \lambda_\varphi \frac{\partial (\rho c)}{\partial \varphi} \right) \dot{\varphi}$$
$$+ \left(\frac{\partial f}{\partial \nabla \varphi} \right) (\nabla \varphi)^{\cdot} + \operatorname{div} \left(\mathbf{T} \cdot \mathbf{v} - \lambda_\varphi \mathbf{J} - \mathbf{J}_e \right) - \widetilde{\mathbf{S}} : \nabla \mathbf{v} + \nabla \lambda_\varphi \cdot \mathbf{J} \leq 0,$$

where we have used $\operatorname{div} \mathbf{v} = 0$. Making use of (2.12) we conclude that the latter inequality is equivalent to

$$-\mathcal{D} = \left(\frac{\partial f}{\partial \varphi} - \frac{\partial \rho}{\partial \varphi} \frac{|\mathbf{v}|^2}{2} - \lambda_\varphi \frac{\partial (\rho c)}{\partial \varphi} - \operatorname{div} \left(\frac{\partial f}{\partial \nabla \varphi} \right) \right) \dot{\varphi} \qquad (2.33)$$
$$+ \operatorname{div} \left(\mathbf{T} \cdot \mathbf{v} - \lambda_\varphi \mathbf{J} + \frac{\partial f}{\partial \nabla \varphi} \dot{\varphi} - \mathbf{J}_e \right) - \left(\widetilde{\mathbf{S}} + \nabla \varphi \otimes \frac{\partial f}{\partial \nabla \varphi} \right) : \nabla \mathbf{v} + \nabla \lambda_\varphi \cdot \mathbf{J} \leq 0,$$

where again the equation $\operatorname{div} \mathbf{v} = 0$ was used.

If we assume now that $\widetilde{\mathbf{S}}, \lambda_\varphi$, and $\mathbf{T} \cdot \mathbf{v} - \lambda_\varphi \mathbf{J} + \frac{\partial f}{\partial \nabla \varphi} \dot{\varphi} - \mathbf{J}_e$ are independent of $\dot{\varphi}$, we conclude that the first term after the equality sign in (2.33) has to vanish for all values of $\dot{\varphi}$. Thus

$$\lambda_\varphi \frac{\partial (\rho c)}{\partial \varphi} = \frac{\partial f}{\partial \varphi} - \frac{\partial \rho}{\partial \varphi} \frac{|\mathbf{v}|^2}{2} - \operatorname{div} \left(\frac{\partial f}{\partial \nabla \varphi} \right).$$

If we denote $\lambda_\varphi = \mu$, then we obtain the same identity for the "chemical potential" μ as before. Moreover, if we now specify the energy flux as

$$\mathbf{J}_e = \mathbf{T} \cdot \mathbf{v} - \mu \mathbf{J} + \frac{\partial f}{\partial \nabla \varphi} \dot{\varphi},$$

we end up with the local dissipation inequality

$$\mathcal{D} = \left(\widetilde{\mathbf{S}} + \nabla \varphi \otimes \frac{\partial f}{\partial \nabla \varphi} \right) : D\mathbf{v} - \nabla \mu \cdot \mathbf{J} \geq 0,$$

which is just (2.16). Thus we can derive the model (2.17)-(2.20) as before by making the same constitutive assumptions.

3 Onsager's Variational Principle – a Third Approach to Derive Thermodynamically Consistent Models

In this section, we follow a third pathway to obtain diffuse interface models in the spirit of (2.25)-(2.27) and in agreement with the postulations of thermodynamics. It

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is based on Onsager's variational principle, see [27] and [11], [16], [28] for applications in multi-phase flow. To widen the range of applications, we discuss two additional features. We allow for gravitational forces or, alternatively, we include the transport of a soluble species across fluidic interfaces as an additional effect. For simplicity, we refrain ourselves in the second case to a species that does not influence the surface tension at the interface. Adopting the notation from the previous sections, the order parameter will be denoted by φ and we take it to be the difference $u_2 - u_1$, of the volume fractions u_j, $j = 1, 2$, of the two liquids involved. Hence,

$$\rho(\varphi) = \frac{\tilde{\rho}_2 - \tilde{\rho}_1}{2}\varphi + \frac{\tilde{\rho}_1 + \tilde{\rho}_2}{2} \tag{3.1}$$

where $\tilde{\rho}_1$ and $\tilde{\rho}_2$ are the specific densities of liquid 1 and 2, respectively. With w, we denote the mass density of the soluble species which we assume to be dilute.

Our starting point is the following set of general evolution equations, see Section 2,

$$\partial_t(\rho\mathbf{v}) + \text{div}(\rho\mathbf{v} \otimes \mathbf{v}) - \text{div }\mathbf{S} + \nabla p = \mathbf{K}, \tag{3.2}$$
$$\text{div }\mathbf{v} = 0, \tag{3.3}$$
$$\partial_t\varphi + \mathbf{v} \cdot \nabla\varphi + \text{div }\mathbf{J}_\varphi = 0, \tag{3.4}$$
$$\partial_t w + \mathbf{v} \cdot \nabla w + \text{div }\mathbf{J}_w = 0 \tag{3.5}$$

with $\rho(\cdot)$ as in (3.1) and $\mathbf{J}_\varphi = \left(\frac{\tilde{\rho}_1 + \tilde{\rho}_2}{2}\right)^{-1}\mathbf{J}$ is a rescaled flux, compare the discussion after (2.28). The stress tensor $\mathbf{S}$ is symmetric (due to conservation of angular momentum), and $\mathbf{K}$ denotes the force density. The additional equation (3.5) is the mass balance of the soluble species and $\mathbf{J}_w$ is the corresponding mass flux. These equations are supposed to hold in a space-time cylinder $\Omega \times (0, T)$ with $\Omega \subset \mathbb{R}^d$ being the domain where the process takes place. Conservation of mass requires that the normal components of $\mathbf{J}_\varphi$ and of $\mathbf{J}_w$ vanish on $\partial\Omega$. As free energy, we choose

$$\int_\Omega f(\varphi, \nabla\varphi)\,dx + \int_\Omega \{g(w) + \beta(\varphi)w\}\,dx$$

with $f(z, p) = f_1(z) + f_2(p)$. Here, $g(\cdot)$ is an entropic term, and $\beta(\varphi)$ attains for $\varphi \leq -1$ or $\varphi \geq 1$ the values β_1 or β_2, respectively. In a sharp-interface limit, these parameters will reappear through the Henry jump condition

$$\frac{w_1}{w_2} = \exp(\beta_2 - \beta_1) \tag{3.6}$$

at the interface separating the two phases (cf. Subsection 4.3.4). The total energy is given by the sum of kinetic and free energy, hence

$$F = \int_\Omega \frac{\rho(\varphi)}{2}|\mathbf{v}|^2\,dx + \int_\Omega f(\varphi, \nabla\varphi)\,dx + \int_\Omega \{g(w) + \beta(\varphi)w\}\,dx.$$

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The time derivative of the free energy is given as

$$\frac{dF}{dt} = \frac{1}{2} \int_\Omega \frac{\partial \rho}{\partial \varphi} |\mathbf{v}|^2 \partial_t \varphi \, dx + \int_\Omega \frac{\partial f}{\partial \varphi} \partial_t \varphi \, dx - \int_\Omega \operatorname{div} \left(\frac{\partial f}{\partial \nabla \varphi} \right) \partial_t \varphi \, dx + \int_\Omega \rho(\varphi) \mathbf{v} \cdot \partial_t \mathbf{v} \, dx$$
$$+ \int_\Omega (g'(w) + \beta(\varphi)) \partial_t w \, dx + \int_\Omega \beta'(\varphi) w \partial_t \varphi \, dx,$$

where we assumed that the normal part of $\frac{\partial f}{\partial \nabla \varphi}$ vanishes on $\partial \Omega$. Observe that

$$\partial_t \mathbf{v} = \frac{1}{\rho} \left\{ \mathbf{K} + \operatorname{div} \mathbf{S} - \frac{\partial \rho}{\partial \varphi} \partial_t \varphi \, \mathbf{v} - \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v}) - \nabla p \right\}$$

and

$$- \int_\Omega \mathbf{v} \cdot \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v}) \, dx = - \int_\Omega \frac{1}{2} |\mathbf{v}|^2 \mathbf{v} \cdot \nabla \rho \, dx$$

if $\mathbf{v} \equiv 0$ on $\partial \Omega$. The last identity follows from integration by parts using $\operatorname{div} \mathbf{v} = 0$. Inserting the evolution equations and integrating by parts gives, assuming $\mathbf{v} \equiv 0$ on $\partial \Omega$,

$$\frac{d}{dt} F = -\frac{1}{2} \int_\Omega \frac{\partial \rho}{\partial \varphi} |\mathbf{v}|^2 (\mathbf{v} \cdot \nabla \varphi + \operatorname{div} \mathbf{J}_\varphi) \, dx - \int_\Omega \frac{\partial f}{\partial \varphi} (\mathbf{v} \cdot \nabla \varphi + \operatorname{div} \mathbf{J}_\varphi) \, dx$$
$$+ \int_\Omega \operatorname{div} \left(\frac{\partial f}{\partial \nabla \varphi} \right) (\mathbf{v} \cdot \nabla \varphi + \operatorname{div} \mathbf{J}_\varphi) \, dx - \int_\Omega \beta'(\varphi) w (\mathbf{v} \cdot \nabla \varphi + \operatorname{div} \mathbf{J}_\varphi) \, dx$$
$$+ \int_\Omega \mathbf{v} \cdot \left\{ \mathbf{K} + \operatorname{div} \mathbf{S} - \frac{\partial \rho}{\partial \varphi} \partial_t \varphi \, \mathbf{v} - \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v}) - \nabla p \right\} \, dx$$
$$- \int_\Omega (g'(w) + \beta(\varphi)) (\mathbf{v} \cdot \nabla w + \operatorname{div} \mathbf{J}_w) \, dx$$
$$= \int_\Omega \mathbf{v} \cdot \nabla \varphi \left\{ \frac{1}{2} \frac{\partial \rho}{\partial \varphi} |\mathbf{v}|^2 - \frac{\partial f}{\partial \varphi} + \operatorname{div} \left(\frac{\partial f}{\partial \nabla \varphi} \right) - \beta'(\varphi) w \right\} \, dx$$
$$+ \int_\Omega \mathbf{v} \cdot \mathbf{K} \, dx - \frac{1}{2} \int_\Omega \mathbf{v} \cdot \nabla \varphi \frac{\partial \rho}{\partial \varphi} |\mathbf{v}|^2 \, dx - \int_\Omega \mathbf{v} \cdot \nabla w \, (g'(w) + \beta(\varphi)) \, dx$$
$$+ \int_\Omega \mathbf{J}_\varphi \cdot \nabla \mu_\varphi \, dx - \int_\Omega D\mathbf{v} : \mathbf{S} \, dx + \int_\Omega \mathbf{J}_w \cdot \nabla \mu_w \, dx.$$

Here, we used

$$- \int_\Omega |\mathbf{v}|^2 \frac{\partial \rho}{\partial \varphi} \partial_t \varphi \, dx = \int_\Omega (\mathbf{v} \cdot \nabla \varphi + \operatorname{div} \mathbf{J}_\varphi) \frac{\partial \rho}{\partial \varphi} |\mathbf{v}|^2 \, dx$$

and we abbreviated

$$\mu_\varphi := -\operatorname{div} \left(\frac{\partial f}{\partial \nabla \varphi} \right) + \frac{\partial f}{\partial \varphi} - \frac{1}{2} \frac{\partial \rho}{\partial \varphi} |\mathbf{v}|^2 + \beta'(\varphi) w$$

and

$$\mu_w := g'(w) + \beta(\varphi)$$

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to denote the chemical potentials corresponding to φ and w, respectively. Recall that in general entropy production is due to external force fields and to gradients of velocity and of chemical potentials, see [8], Chapter 3. However, if the specific densities of the external forces[2] acting on the different species are identical, then those forces do not contribute to entropy production. Therefore, if no other external forces than gravity forces are applied, we may identify the rate of change of the mechanical work with

$$\frac{dW}{dt} = -\int_\Omega \mathbf{v}\cdot\nabla\varphi\mu_\varphi\,dx - \int_\Omega \mathbf{v}\cdot\nabla w\mu_w\,dx + \int_\Omega \mathbf{v}\cdot\mathbf{K}\,dx - \frac{1}{2}\int_\Omega \mathbf{v}\cdot\nabla\varphi\frac{\partial\rho}{\partial\varphi}|\mathbf{v}|^2\,dx. \quad (3.7)$$

As

$$\frac{dW}{dt} = \begin{cases} \int_\Omega \mathbf{K}_{\text{grav}}\cdot\mathbf{v}\,dx & \text{case with gravitational forces} \\ 0 & \text{case with soluble species,} \end{cases}$$

equation (3.7) is satisfied if

$$\mathbf{K} = \begin{cases} \mu_\varphi\nabla\varphi + \frac{1}{2}\frac{\partial\rho}{\partial\varphi}|\mathbf{v}|^2\nabla\varphi + \mathbf{K}_{\text{grav}} & \text{case with gravitational forces,} \\ \mu_\varphi\nabla\varphi + \mu_w\nabla w + \frac{1}{2}\frac{\partial\rho}{\partial\varphi}|\mathbf{v}|^2\nabla\varphi & \text{case with soluble species.} \end{cases}$$

Here, $\mathbf{K}_{\text{grav}}$ denotes the gravitational force.

To determine the fluxes $\mathbf{J}_\varphi, \mathbf{J}_w$ and the stress tensor $\mathbf{S}$, we introduce the dissipation functional

$$\Phi(\mathbf{J}_\varphi, \mathbf{J}_w, \mathbf{S}) := \int_\Omega \left\{ \frac{|\mathbf{J}_\varphi|^2}{2M(\varphi)} + \frac{|\mathbf{S}|^2}{4\eta(\varphi)} + \frac{|\mathbf{J}_w|^2}{2K(\varphi)w} \right\}\,dx.$$

We use Onsager's variational principle which postulates

$$\delta_{(\mathbf{J}_\varphi, \mathbf{J}_w, \mathbf{S})}\left(\frac{dF}{dt}(\mathbf{J}_\varphi, \mathbf{J}_w, \mathbf{S}) + \Phi(\mathbf{J}_\varphi, \mathbf{J}_w, \mathbf{S}) \right) \overset{!}{=} 0.$$

This gives $\mathbf{J}_\varphi = -M(\varphi)\nabla\mu_\varphi$, $\mathbf{J}_w = -K(\varphi)w\nabla\mu_w$, and $\mathbf{S} = 2\eta(\varphi)\frac{\nabla\mathbf{v}+\nabla\mathbf{v}^T}{2}$. Altogether, when a soluble species is around, we end up with

$$\partial_t(\rho\mathbf{v}) + \text{div}(\rho\mathbf{v}\otimes\mathbf{v})$$
$$- \text{div}\left(2\eta(\varphi)D\mathbf{v}\right) + \nabla p = \mu_\varphi\nabla\varphi + \mu_w\nabla w + \frac{1}{2}\frac{\partial\rho}{\partial\varphi}|\mathbf{v}|^2\nabla\varphi, \quad (3.8)$$
$$\text{div}\,\mathbf{v} = 0, \quad (3.9)$$
$$\partial_t\varphi + \mathbf{v}\cdot\nabla\varphi - \text{div}\left(M(\varphi)\nabla\mu_\varphi\right) = 0, \quad (3.10)$$
$$\partial_t w + \mathbf{v}\cdot\nabla w - \text{div}\left(K(\varphi)w\nabla\mu_w\right) = 0, \quad (3.11)$$
$$\mu_\varphi = -\text{div}\left(\frac{\partial f}{\partial\nabla\varphi}\right) + \frac{\partial f}{\partial\varphi} - \frac{1}{2}\frac{\partial\rho}{\partial\varphi}|\mathbf{v}|^2 + \beta'(\varphi)w, \quad (3.12)$$
$$\mu_w = g'(w) + \beta(\varphi) \quad (3.13)$$

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[2]i.e. the quotient of force density and mass density

where $D\mathbf{v} = \frac{1}{2}\left(\nabla\mathbf{v} + \nabla\mathbf{v}^T\right)$ and $\rho(\varphi) = \frac{\tilde{\rho}_2 - \tilde{\rho}_1}{2}\varphi + \frac{\tilde{\rho}_1 + \tilde{\rho}_2}{2}$. The evolution equation for w becomes

$$\partial_t w + \mathbf{v}\cdot\nabla w = \operatorname{div}(K(\varphi)w\nabla(g'(w) + \beta(\varphi))). \tag{3.14}$$

In the case of gravitational forces, the system has to be changed accordingly.

Remarks:

- If we choose $g(w) = w(\log w - 1)$, the equations (3.11),(3.13) result in the diffusion equation

$$\partial_t w + \mathbf{v}\cdot\nabla w = \operatorname{div}(K(\varphi)(\nabla w + w\nabla\beta(\varphi))).$$

- The interfacial force term $\mathbf{K} = \mu_\varphi\nabla\varphi + \mu_w\nabla w + \frac{1}{2}\frac{\partial\rho}{\partial\varphi}|\mathbf{v}|^2\nabla\varphi$ can equivalently be written as

$$\nabla(f(\varphi,\nabla\varphi) + g(w) + \beta(\varphi)w) - \operatorname{div}\left(\nabla\varphi\otimes\frac{\partial f(\varphi,\nabla\varphi)}{\partial\nabla\varphi}\right).$$

  Here, the first term is of pressure type whereas $\nabla\varphi\otimes\frac{\partial f}{\partial\nabla\varphi}$ provides an additional stress tensor contribution representing interfacial forces. We can hence conclude that the derivations in Sections 2 and 3 up to a reinterpretation of the pressure lead to the same diffuse interface model. The analogous observation for "Model H" has been already discussed in [20].

- It is also possible to derive (3.8)-(3.13) with the approaches discussed in Section 2.

- Taking the definitions of μ_φ and $\mathbf{K}$ into account, we observe that $\mathbf{K}$ in fact does not depend on $\mathbf{v}$.

4 Sharp interface asymptotics

In this section we identify the sharp interface limit of the diffuse interface model introduced in the preceding sections. We will use the method of formally matched asymptotic expansions where asymptotic expansions in bulk regions have to match with expansions in interfacial regions. There are four different asymptotic limits of interest. Two use a constant mobility and will either lead to a model where diffusion takes place through the bulk or to a model without any diffusion through the bulk, see also Abels and Röger [3] for the case when the densities in the two fluids are the same. Two cases are based on a mobility which is zero when the phase field takes the values ± 1. In this case one of course does not observe diffusion through the bulk in the sharp interface limit. But depending on the scaling we will either see surface diffusion along the interface or not.

4.1 The governing equations

As usual for phase field models we introduce a scaling for f with respect to a small length scale parameter ε as follows

$$f(\varphi, \nabla\varphi) = \frac{\hat{\sigma}\varepsilon}{2}|\nabla\varphi|^2 + \frac{\hat{\sigma}}{\varepsilon}\psi(\varphi)$$

where $\hat{\sigma}$ is a constant related to the surface energy density. As in Section 3, we choose the difference of volume fractions as order parameter and we consider the following system

$$\partial_t(\rho\mathbf{v}) + \operatorname{div}(\rho\mathbf{v}\otimes\mathbf{v}) - \operatorname{div}(2\eta(\varphi)D\mathbf{v}) + \nabla p = -\hat{\sigma}\varepsilon\operatorname{div}(\nabla\varphi\otimes\nabla\varphi)\,, \qquad (4.1)$$

$$\operatorname{div}\mathbf{v} = 0\,, \qquad (4.2)$$

$$\partial_t\varphi + \mathbf{v}\cdot\nabla\varphi = \operatorname{div}(m_\varepsilon(\varphi)\nabla\mu)\,, \qquad (4.3)$$

$$\mu = \frac{\hat{\sigma}}{\varepsilon}\psi'(\varphi) - \hat{\sigma}\varepsilon\Delta\varphi - \rho'(\varphi)\tfrac{1}{2}|\mathbf{v}|^2 + \beta'(\varphi)w\,, \qquad (4.4)$$

$$\partial_t w + \mathbf{v}\cdot\nabla w = \operatorname{div}(K(\varphi)w\nabla(g'(w) + \beta(\varphi)))\,. \qquad (4.5)$$

To simplify the notation we drop the φ as index in the chemical potential. We assume that

- $\rho(\varphi) = \frac{\tilde{\rho}_2 - \tilde{\rho}_1}{2}\varphi + \frac{\tilde{\rho}_1 + \tilde{\rho}_2}{2}$,

- g is convex,

- $\beta(\varphi)$ is smooth with $\beta(1) = \beta_2$, $\beta(-1) = \beta_1$,

- $\eta(\varphi)$ is smooth and positive with $\eta(1) = \eta_2$, $\eta(-1) = \eta_1$,

- $\psi(\varphi)$ is a double-well potential such that $\psi(1) = \psi(-1) = 0$ and $\psi(z) > 0$ if $z \notin \{1, -1\}$,

- $K(\varphi)$ is smooth such that $K(1) = K_2$, $K(-1) = K_1$.

For the mobility m_ε we distinguish four cases:

$$m_\varepsilon(\varphi) = \begin{cases} m_0 & \text{case I}\,, \\ \varepsilon m_0 & \text{case II}\,, \\ \frac{m_1}{\varepsilon}(1 - \varphi^2)_+ & \text{case III}\,, \\ m_1(1 - \varphi^2)_+ & \text{case IV} \end{cases}$$

where $m_0, m_1 > 0$ are constants and $(.)_+$ is the positive part of the quantity in the brackets. The total relevant energy in this scaling is

$$F_\varepsilon(\varphi, \mathbf{v}, w) = \int_\Omega \left\{ \frac{\rho(\varphi)}{2}|\mathbf{v}|^2 + \frac{\varepsilon\hat{\sigma}}{2}|\nabla\varphi|^2 + \frac{\hat{\sigma}}{\varepsilon}\psi(\varphi) + g(w) + \beta(\varphi)w \right\} dx\,.$$

For a solution $(\mathbf{v}^\varepsilon, p^\varepsilon, \varphi^\varepsilon, \mu^\varepsilon, w^\varepsilon)$ of the system (4.1)-(4.5) we perform formally matched asymptotic expansions. It will turn out that the phase field φ^ε will change its values rapidly on a length scale proportional to ε. For additional information on asymptotic expansions for phase field equations we refer to [15, 17].

4.2 Outer expansions

We first expand the solution in outer regions away from the interface. We assume an expansion of the form $\mathbf{v}^\varepsilon = \sum_{k=0}^\infty \varepsilon^k \mathbf{v}_k$, $\varphi^\varepsilon = \sum_{k=0}^\infty \varepsilon^k \varphi_k, \ldots$. An expansion of (4.4) in outer regions gives to leading order $\psi'(\varphi_0) = 0$ and we obtain the stable solutions ± 1. We will denote by $\Omega^\pm$ the regions where $\varphi_0 = \pm 1$. The leading order expansion of the other equations are straightforward. We obtain:

$$\rho_i(\partial_t \mathbf{v}_0 + \operatorname{div}(\mathbf{v}_0 \otimes \mathbf{v}_0)) - 2\eta_i \operatorname{div} D\mathbf{v}_0 + \nabla p_0 = 0 \,, \tag{4.6}$$

$$\operatorname{div} \mathbf{v}_0 = 0 \,, \tag{4.7}$$

$$\text{in case I} \qquad \Delta \mu_0 = 0 \,, \tag{4.8}$$

$$\partial_t w_0 + \mathbf{v}_0 \cdot \nabla w_0 = K_i \nabla \cdot (w_0 \nabla g'(w_0)) \,, \tag{4.9}$$

where $i = 1, 2$ for $x \in \Omega_-, \Omega_+$ and $\rho_1 = \rho(-1) = \tilde\rho_1, \rho_2 = \rho(1) = \tilde\rho_2$. Due to the divergence free velocity we obtain $2 \operatorname{div} D\mathbf{v}_0 = \Delta \mathbf{v}_0$ and hence (4.6) simplifies to

$$\rho_i(\partial_t \mathbf{v}_0 + \operatorname{div}(\mathbf{v}_0 \otimes \mathbf{v}_0)) - \eta_i \Delta \mathbf{v}_0 + \nabla p_0 = 0 \,.$$

We remark that (4.9) leads to the convection diffusion equation

$$\partial_t w_0 + \mathbf{v}_0 \cdot \nabla w_0 = K_i \Delta w_0$$

in the case that $g(w) = w(\log w - 1)$. In the cases II-IV we will not need the chemical potential μ in the bulk.

4.3 Inner expansions

We now make an expansion in an interfacial region where a transition between two phases takes place.

4.3.1 New coordinates in the inner region

Denoting by $\Gamma = (\Gamma(t))_{t \geq 0}$ the smoothly evolving interface which we expect to be obtained in the limit when ε tends to zero, we now introduce new coordinates in a neighborhood of Γ. Choosing a time interval $I \subset \mathbb{R}$ and a spatial parameter domain $U \subset \mathbb{R}^{d-1}$ we define a local parameterization

$$\boldsymbol{\gamma} : I \times U \to \mathbb{R}^d$$

of Γ. By $\boldsymbol{\nu}$ we denote the unit normal to $\Gamma(t)$ pointing into phase 2 (which is the phase related to $\varphi = 1$). Close to $\boldsymbol{\gamma}(I \times U)$ we consider the signed distance function

$d(t, x)$ of a point x to $\Gamma^0(t)$ with $d(t, x) > 0$ if $x \in \Omega^+(t)$. We now introduce a local parameterization of $I \times \mathbb{R}^d$ close to $\boldsymbol{\gamma}(I \times U)$ using the rescaled distance $z = \frac{d}{\varepsilon}$ as follows

$$G^\varepsilon(t, s, z) := (t, \boldsymbol{\gamma}(t, s) + \varepsilon z \boldsymbol{\nu}(t, s)).$$

We denote by

$$\mathcal{V} = \partial_t \boldsymbol{\gamma} \cdot \boldsymbol{\nu}$$

the (scalar) normal velocity and observe that the inverse function $(t, s, z)(t, x) := (G^\varepsilon)^{-1}(t, x)$ fulfills

$$\partial_t z = \tfrac{1}{\varepsilon} \partial_t d = -\tfrac{1}{\varepsilon} \mathcal{V}.$$

To derive the last identity we used (2.6) and (2.20) of [7]. For a scalar function $b(t, x)$ we obtain for $\hat{b}$ defined in the new coordinates via $\hat{b}(t, s(t, x), z(t, x)) = b(t, x)$ the identity

$$\frac{d}{dt} b(t, x) = \partial_t z \partial_z \hat{b} + \partial_t s \cdot \nabla_s \hat{b} + \partial_t \hat{b} = -\tfrac{1}{\varepsilon} \mathcal{V} \partial_z \hat{b} + \text{ h.o.t.}$$

where h.o.t. stands for higher order terms. With respect to the spatial variables we obtain, see Appendix,

$$\nabla_x b = \nabla_{\Gamma_{\varepsilon z}} \hat{b} + \tfrac{1}{\varepsilon} \partial_z \hat{b} \, \boldsymbol{\nu} \tag{4.10}$$

where $\nabla_{\Gamma_{\varepsilon z}}$ is the tangential gradient on

$$\Gamma_{\varepsilon z} := \{\boldsymbol{\gamma}(s) + \varepsilon z \boldsymbol{\nu}(s) \mid s \in U\}$$

where here and in what follows we often omit the t-dependence. For a vector quantity $\mathbf{j}(t, x)$ written in the new coordinates via $\hat{\mathbf{j}}(t, s(t, x), z(t, x)) = \mathbf{j}(t, x)$ we obtain

$$\nabla_x \cdot \mathbf{j} = \nabla_{\Gamma_{\varepsilon z}} \cdot \hat{\mathbf{j}} + \tfrac{1}{\varepsilon} \partial_z \hat{\mathbf{j}} \cdot \boldsymbol{\nu}, \tag{4.11}$$

where $\nabla_{\Gamma_{\varepsilon z}} \cdot \hat{\mathbf{j}}$ is the divergence of $\hat{\mathbf{j}}$ on $\Gamma_{\varepsilon z}$. In the Appendix we compute

$$\Delta_x b = \Delta_{\Gamma_{\varepsilon z}} \hat{b} - \tfrac{1}{\varepsilon}(\kappa + \varepsilon z |\mathcal{S}|^2) \partial_z \hat{b} + \tfrac{1}{\varepsilon^2} \partial_{zz} \hat{b} + \text{ h.o.t.}, \tag{4.12}$$

where κ is the mean curvature (the sum of the principal curvatures) and $|\mathcal{S}|$ is the spectral norm of the Weingarten map $\mathcal{S}$. In addition we note that (see Appendix)

$$\begin{aligned}
\nabla_{\Gamma_{\varepsilon z}} \hat{b}(s, z) &= \nabla_\Gamma \hat{b}(s, z) + \text{ h.o.t.}, \\
\nabla_{\Gamma_{\varepsilon z}} \cdot \hat{\mathbf{j}}(s, z) &= \nabla_\Gamma \cdot \hat{\mathbf{j}}(s, z) + \text{ h.o.t.}, \\
\Delta_{\Gamma_{\varepsilon z}} \hat{b}(s, z) &= \Delta_\Gamma \hat{b}(s, z) + \text{ h.o.t.}
\end{aligned}$$

where $\nabla_\Gamma, \nabla_\Gamma \cdot, \Delta_\Gamma$ are the surface gradient, the surface divergence and the surface Laplacian on Γ.

4.3.2 Matching conditions

We now assume an ε-series approximation of the unknown functions $\varphi, \mu, \mathbf{v}, p, w, \ldots$ which in the inner variables we will denote by $\Phi, M, \mathbf{V}, P, W, \ldots$. Denoting by $\Phi_0 + \varepsilon \Phi_1 + \ldots$ the inner expansion and by $\varphi_0 + \varepsilon \varphi_1 + \ldots$ the outer expansion of the phase field we obtain the following matching conditions at $x = \boldsymbol{\gamma}(s)$:

$$\lim_{z \to \pm\infty} \Phi_0(z, s) = \varphi_0(x\pm), \tag{4.13}$$

$$\lim_{z \to \pm\infty} \partial_z \Phi_1(z, s) = \nabla \varphi_0(x\pm) \cdot \boldsymbol{\nu} \tag{4.14}$$

for $z \to \pm\infty$, where $\varphi_0(x\pm), \ldots$ denotes the limit $\lim_{\delta \searrow 0} \varphi_0(x \pm \delta\boldsymbol{\nu})$. In addition we obtain that if $\Phi_1(z, s) = A_\pm(s) + B_\pm(s)z + o(1)$ as $z \to \pm\infty$ the identities

$$A_\pm(s) = \varphi_1(x\pm), \;\; B_\pm(s) = \nabla \varphi_0(x\pm) \cdot \boldsymbol{\nu} \tag{4.15}$$

have to hold (see [14], [18]). Of course similar relations hold for the other functions like $\mathbf{v}, \mu, \ldots$.

4.3.3 Deriving the sharp interface limit

Plugging the asymptotic expansions into (4.1)-(4.5) we ask that each individual coefficient of a power in ε vanishes. The equation (4.4) gives to leading order $\frac{1}{\varepsilon}$:

$$0 = \partial_{zz}\Phi_0 - \psi'(\Phi_0) \tag{4.16}$$

and from (4.13) we obtain

$$\Phi_0(z) \to \pm 1 \quad \text{for} \quad z \to \pm\infty. \tag{4.17}$$

We now choose the unique solution of (4.16), (4.17) which fulfills

$$\Phi_0(0) = 0.$$

We in particular obtain that Φ_0 does not depend on t and s. Equation (4.2) gives to leading order

$$\partial_z \mathbf{V}_0 \cdot \boldsymbol{\nu} = \partial_z(\mathbf{V}_0 \cdot \boldsymbol{\nu}) = 0. \tag{4.18}$$

The matching condition requires that $(\mathbf{V}_0 \cdot \boldsymbol{\nu})(z)$ is bounded. Hence

$$(\mathbf{v}_0 \cdot \boldsymbol{\nu}_0)(x+) = \lim_{z \to \infty}(\mathbf{V} \cdot \boldsymbol{\nu}_0)(z) = \lim_{z \to -\infty}(\mathbf{V} \cdot \boldsymbol{\nu}_0)(z) = (\mathbf{v} \cdot \boldsymbol{\nu}_0)(x-).$$

This implies

$$[\mathbf{v}_0 \cdot \boldsymbol{\nu}]_-^+ = 0,$$

where $[u]_-^+(x) = u(x+) - u(x-)$ denotes the jump of a quantity at the interface. Applying (4.10) for each component we obtain

$$\nabla_x \mathbf{v} = \tfrac{1}{\varepsilon}\partial_z \mathbf{V} \otimes \boldsymbol{\nu} + \nabla_{\Gamma_{\varepsilon z}}\mathbf{V},$$

$$D_x \mathbf{v} = \tfrac{1}{2}\tfrac{1}{\varepsilon}(\partial_z \mathbf{V} \otimes \boldsymbol{\nu} + \boldsymbol{\nu} \otimes \partial_z \mathbf{V}) + \tfrac{1}{2}(\nabla_{\Gamma_{\varepsilon z}}\mathbf{V} + (\nabla_{\Gamma_{\varepsilon z}}\mathbf{V})^\top).$$

Defining $\mathcal{E}(\mathbf{A}) = \frac{1}{2}(\mathbf{A} + \mathbf{A}^\top)$ for a quadratic matrix $\mathbf{A}$ we compute

$$\begin{aligned}
\nabla_x \cdot (\eta(\varphi) D_x \mathbf{v}) &= \tfrac{1}{\varepsilon^2}\partial_z(\eta(\Phi)\mathcal{E}(\partial_z \mathbf{V} \otimes \boldsymbol{\nu}))\boldsymbol{\nu} + \tfrac{1}{\varepsilon}\partial_z(\eta(\Phi)\mathcal{E}(\nabla_{\Gamma_{\varepsilon z}}\mathbf{V}))\boldsymbol{\nu} \\
&\quad + \tfrac{1}{\varepsilon}\nabla_{\Gamma_{\varepsilon z}} \cdot (\eta(\Phi)\mathcal{E}(\partial_z\mathbf{V} \otimes \boldsymbol{\nu})) + \nabla_{\Gamma_{\varepsilon z}} \cdot (\eta(\Phi)\mathcal{E}(\nabla_{\Gamma_{\varepsilon z}}\mathbf{V})) \\
&= \tfrac{1}{\varepsilon^2}\partial_z(\eta(\Phi)\mathcal{E}(\partial_z\mathbf{V} \otimes \boldsymbol{\nu})\boldsymbol{\nu}) + \tfrac{1}{\varepsilon}\partial_z(\eta(\Phi)\mathcal{E}(\nabla_{\Gamma_{\varepsilon z}}\mathbf{V})\boldsymbol{\nu}) \\
&\quad + \tfrac{1}{\varepsilon}\nabla_{\Gamma_{\varepsilon z}} \cdot (\eta(\Phi)\mathcal{E}(\partial_z\mathbf{V} \otimes \boldsymbol{\nu})) + \nabla_{\Gamma_{\varepsilon z}} \cdot (\eta(\Phi)\mathcal{E}(\nabla_{\Gamma_{\varepsilon z}}\mathbf{V})),
\end{aligned}$$

where we used $\partial_z \boldsymbol{\nu} = 0$. We conclude from (4.18)

$$(\boldsymbol{\nu} \otimes \partial_z \mathbf{V}_0)\boldsymbol{\nu} = (\partial_z \mathbf{V}_0 \cdot \boldsymbol{\nu})\boldsymbol{\nu} = 0.$$

The fact that Φ_0 does not depend on t and s and (4.10) imply

$$\nabla\varphi \otimes \nabla\varphi = \tfrac{1}{\varepsilon^2}(\partial_z\Phi_0)^2(\boldsymbol{\nu} \otimes \boldsymbol{\nu}) + \tfrac{1}{\varepsilon}\partial_z\Phi_1\partial_z\Phi_0(\boldsymbol{\nu} \otimes \boldsymbol{\nu}) + \text{ h.o.t.}$$

and since $(\nabla_\Gamma \boldsymbol{\nu}) \cdot \boldsymbol{\nu} = 0$ we get

$$\varepsilon\nabla \cdot (\nabla\varphi \otimes \nabla\varphi) = \tfrac{1}{\varepsilon^2}\partial_z(\partial_z\Phi_0)^2\boldsymbol{\nu} + \tfrac{1}{\varepsilon}(\partial_z\Phi_0)^2(\nabla_\Gamma \cdot \boldsymbol{\nu})\boldsymbol{\nu} + \tfrac{1}{\varepsilon}\partial_z(\partial_z\Phi_1\partial_z\Phi_0)\boldsymbol{\nu} + \text{ h.o.t.}.$$

Hence we obtain at the order $\frac{1}{\varepsilon^2}$ from the momentum equation

$$\hat{\sigma}\partial_z(\partial_z\Phi_0)^2\boldsymbol{\nu} + \partial_z(\eta(\Phi_0)\partial_z\mathbf{V}_0) + (\partial_z P_{-1})\boldsymbol{\nu} = 0. \tag{4.19}$$

Multiplying (4.19) with $\boldsymbol{\nu}$, taking $\partial_z\boldsymbol{\nu} = 0$ and $\partial_z\mathbf{V}_0 \cdot \boldsymbol{\nu} = 0$ into account gives

$$\hat{\sigma}\partial_z((\partial_z\Phi_0)^2) + \partial_z P_{-1} = 0.$$

Hence (4.19) implies

$$\partial_z(\eta(\Phi_0)\partial_z\mathbf{V}_0) = 0. \tag{4.20}$$

Matching implies that $\mathbf{V}_0(z)$ is bounded. This implies that (4.20) interpreted as an ODE in z has only solutions $\mathbf{V}_0$ which are constant in z. This implies after matching

$$[\mathbf{v}_0]_-^+ = 0.$$

We now want to analyze the momentum equation to the next order. The term $\nabla \cdot (\eta(\varphi) D\mathbf{v})$ gives to the order $\frac{1}{\varepsilon}$,

$$\partial_z(\eta(\Phi_0)\mathcal{E}(\partial_z\mathbf{V}_1 \otimes \boldsymbol{\nu})\boldsymbol{\nu}) + \partial_z(\eta(\Phi_0)\mathcal{E}(\nabla_\Gamma\mathbf{V}_0)\boldsymbol{\nu}).$$

Matching requires $\lim_{z \to \pm\infty} \partial_z\mathbf{V}_1(z) = \nabla\mathbf{v}_0(x\pm)\boldsymbol{\nu}$ and hence

$$\partial_z\mathbf{V}_1 \otimes \boldsymbol{\nu} + \nabla_\Gamma\mathbf{V}_0 \to \nabla_x\mathbf{v} \quad \text{for} \quad z \to \pm\infty. \tag{4.21}$$

Altogether we obtain for the momentum equation at order $\frac{1}{\varepsilon}$:

$$\begin{aligned}
&- \ \partial_z(\rho(\Phi_0)\mathbf{V}_0)\mathcal{V} + \partial_z(\rho(\Phi_0)(\mathbf{V}_0 \otimes \mathbf{V}_0))\boldsymbol{\nu} \\
&- \ 2\partial_z(\eta(\Phi_0)\mathcal{E}(\partial_z\mathbf{V}_1 \otimes \boldsymbol{\nu})\boldsymbol{\nu}) - 2\partial_z(\eta(\Phi_0)\mathcal{E}(\nabla_\Gamma\mathbf{V}_0)\boldsymbol{\nu}) \\
&- \ \hat{\sigma}(\partial_z\Phi_0)^2\kappa\boldsymbol{\nu} + \hat{\sigma}\partial_z(\partial_z\Phi_1\partial_z\Phi_0)\boldsymbol{\nu} + \partial_z P_0\boldsymbol{\nu} = 0.
\end{aligned}$$

Integrating with respect to z gives after matching and using (4.21)

$$-[\rho_0\mathbf{v}_0]_-^+\mathcal{V} + [\rho_0\mathbf{v}_0]_-^+\mathbf{v}_0\cdot\boldsymbol{\nu} - 2[\eta\mathcal{E}(\nabla_x\mathbf{v}_0)]_-^+\boldsymbol{\nu} - \hat{\sigma}\left(\int_{-\infty}^{\infty}(\partial_z\Phi_0)^2\,dz\right)\kappa\boldsymbol{\nu} + [p_0]_-^+\boldsymbol{\nu} = 0\,.$$

Defining $c_0 := \int_{-\infty}^{\infty}(\partial_z\Phi_0)^2\,dz$ and $\sigma = c_0\hat{\sigma}$ we obtain

$$[\rho_0\mathbf{v}_0]_-^+(\mathbf{v}_0\cdot\boldsymbol{\nu} - \mathcal{V}) - 2[\eta D\mathbf{v}_0]_-^+\boldsymbol{\nu} + [p_0]_-^+\boldsymbol{\nu} = \sigma\kappa\boldsymbol{\nu}\,.$$

4.3.4 The diffusion equations to leading order

The analysis of (4.3) now depends on the ansatz for the mobility. We have to distinguish between four cases.

Case I : $m_\varepsilon(\varphi) = m_0$.
At order $\frac{1}{\varepsilon^2}$ we obtain from (4.3)

$$0 = \partial_z(m_0\partial_z M_0\boldsymbol{\nu})\cdot\boldsymbol{\nu} = m_0\partial_{zz}M_0\,.$$

Matching implies that M_0 is bounded and hence M_0 is constant. In particular we derive
$$[\mu_0]_-^+ = 0\,.$$

Case II : $m_\varepsilon(\varphi) = \varepsilon m_0$.
At order $\frac{1}{\varepsilon}$ we conclude from (4.3)

$$-\mathcal{V}\partial_z\Phi_0 + (\mathbf{v}_0\cdot\boldsymbol{\nu})\partial_z\Phi_0 = \partial_z(m_0\partial_z M_0\boldsymbol{\nu})\cdot\boldsymbol{\nu} = m_0\partial_{zz}M_0\,. \tag{4.22}$$

Since $\mu_{-1} = 0$, we obtain from matching

$$\partial_z M_0 \to 0 \quad\text{for}\quad z \to \pm\infty\,.$$

Integrating (4.22) with respect to z gives

$$\mathcal{V} = \mathbf{v}_0\cdot\boldsymbol{\nu}\,.$$

In addition we get $\partial_{zz}M_0 = 0$ and hence M_0 does not depend on z.

Case III : $m_\varepsilon(\varphi) = m_1(1 - \varphi^2)_+$.
At order $\frac{1}{\varepsilon^2}$ we get

$$0 = \partial_z(m_1(1 - \Phi_0^2)\partial_z M_0\boldsymbol{\nu})\cdot\boldsymbol{\nu} = \partial_z(m_1(1 - \Phi_0^2)\partial_z M_0)\,.$$

Matching implies
$$m_1(1 - \Phi_0^2)\partial_z M_0 \to 0 \quad\text{for}\quad z \to \pm\infty\,.$$

We hence obtain
$$m_1(1 - \Phi_0^2)\partial_z M_0 \equiv 0,$$

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which implies
$$M_0 = M_0(s,t) \,.$$

Case IV : $m_\varepsilon(\varphi) = \varepsilon m_1(1 - \varphi^2)_+ \,.$

At order $\frac{1}{\varepsilon}$ we get

$$-\mathcal{V}\partial_z\Phi_0 + (\mathbf{V_0}) \cdot \boldsymbol{\nu}\partial_z\Phi_0 = \partial_z(m_1(1 - \Phi_0^2)\partial_z M_0)$$

and hence combining arguments from the Cases II and III above we obtain

$$\mathcal{V} = \mathbf{v}_0 \cdot \boldsymbol{\nu} \quad \text{and} \quad M_0 = M_0(s,t) \,.$$

We now analyze the diffusion equation for the soluble species. Equation (4.5) gives to leading order $\frac{1}{\varepsilon^2}$

$$\partial_z(K(\Phi_0)W_0\partial_z(g'(W_0 + \beta(\Phi_0)))) = 0 \,. \tag{4.23}$$

Matching to the outer solution gives that $g'(W_0) + \beta(\Phi_0)$ is bounded. Multiplying (4.23) by $g'(W_0) + \beta(\Phi_0)$, integration and integration by parts gives

$$\int_{-\infty}^{\infty} K(\Phi_0)W_0|\partial_z(g'(W_0) + \beta(\Phi_0))|^2 dz = 0 \,.$$

Assuming $W_0 > 0$ we obtain that

$$g'(W_0) + \beta(\Phi_0)$$

does not depend on z. Hence

$$[g'(w_0) + \beta(\varphi_0)]_-^+ = 0 \,.$$

This implies

$$\log w_0(x+) - \log w_0(x-) + \beta_2 - \beta_1 = 0$$

which yields the Henry jump condition

$$\frac{w_0(x-)}{w_0(x+)} = \exp(\beta_2 - \beta_1) \,.$$

4.3.5 The generalized Gibbs–Thomson equation

The equation for the chemical potential gives to the order ε^0

$$M_0 = \hat{\sigma}\psi''(\Phi_0)\Phi_1 - \hat{\sigma}\partial_{zz}\Phi_1 + \hat{\sigma}\partial_z\Phi_0\kappa - \tfrac{1}{2}\rho'(\Phi_0)|\mathbf{V}_0|^2 + \beta'(\Phi_0)W_0 \,. \tag{4.24}$$

In order to be able to obtain a solution Φ_1 from (4.24) a solvability condition has to hold. This solvability condition will yield the generalized Gibbs–Thomson equation.

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We multiply (4.24) with $\partial_z \Phi_0$, integrate with respect to z and obtain (using the facts that M_0 and V_0 do not depend on z):

$$2M_0 = \hat\sigma \int_{-\infty}^{\infty} (\psi''(\Phi_0)\partial_z\Phi_0\Phi_1 - \partial_{zz}\Phi_1\partial_z\Phi_0)dz$$

$$+\hat\sigma\kappa \int_{-\infty}^{\infty} (\partial_z\Phi_0)^2 dz - \tfrac{1}{2}|\mathbf{V}_0|^2 \int_{-\infty}^{\infty} \partial_z\rho(\Phi_0)dz + \int_{-\infty}^{\infty} \partial_z\beta(\Phi_0)W_0 dz\,.$$

We obtain after integration by parts, using the fact that $\partial_z\Phi_0(z), \partial_{zz}\Phi_0(z)$ decay exponentially for $|z| \to \infty$,

$$2M_0 = \hat\sigma \int_{-\infty}^{\infty} \partial_z(\psi'(\Phi_0) - \partial_{zz}\Phi_0)\Phi_1 dz + \hat\sigma c_0 \kappa - \tfrac{1}{2}|\mathbf{V}_0|^2[\rho_0]_-^+$$

$$+ \int_{-\infty}^{\infty} \partial_z(\beta(\Phi_0)W_0 + g(W_0))dz - \int_{-\infty}^{\infty} (\beta(\Phi_0) + g'(W_0))\partial_z W_0 dz\,.$$

Since $\beta(\Phi_0) + g'(W_0)$ does not depend on z and since $\psi'(\Phi_0) - \partial_{zz}\Phi_0 = 0$, see (4.16), we obtain

$$2\mu_0 = \sigma\kappa - \tfrac{1}{2}|\mathbf{v}_0|^2[\rho_0]_-^+ + [g(w_0) - g'(w_0)w_0]_-^+\,.$$

This identity has been derived for a general function g. In the case $g(w) = w\log w - w$ we obtain

$$2\mu_0 = \sigma\kappa - \tfrac{1}{2}|\mathbf{v}_0|^2[\rho_0]_-^+ - [w_0]_-^+\,.$$

4.3.6 Interfacial flux balance in the sharp interface limit

We now expand the equations (4.3) and (4.5) further in order to obtain contributions of the diffusive fluxes in the interface. The result will depend on the choice of the mobility. In the cases II and IV the interfacial diffusive fluxes for φ are scaled such that they do not contribute to a limiting sharp interface problem. We hence consider only the cases I and III.

Case I : $m_\varepsilon(\varphi) = m_0$.
At order $\frac{1}{\varepsilon}$ we deduce from (4.3)

$$(-\mathcal{V} + \mathbf{V}_0 \cdot \boldsymbol{\nu})\partial_z\Phi_0 = \partial_z(m_0\partial_z M_1)\,. \tag{4.25}$$

Matching gives $\partial_z M_1 \to \nabla\mu_0 \cdot \boldsymbol{\nu}$ for $z \to \pm\infty$. Integrating (4.25) gives

$$2(-\mathcal{V} + \mathbf{v}_0 \cdot \boldsymbol{\nu}) = m_0[\nabla\mu_0 \cdot \boldsymbol{\nu}]_-^+\,.$$

Case III : $m_\varepsilon(\varphi) = \frac{m_1}{\varepsilon}(1 - \varphi^2)_+$.
We have up to order ε^0 in the interfacial region (setting $m(\varphi) = m_1(1 - \varphi^2)$)

$$\nabla \cdot (m(\varphi)\nabla\mu) = \tfrac{1}{\varepsilon^2}\partial_z(m(\Phi_0)\partial_z M_0) +$$
$$\tfrac{1}{\varepsilon}\partial_z(m(\Phi_0)\partial_z M_1 + m'(\Phi_0)\Phi_1\partial_z M_0) + \tfrac{1}{\varepsilon}\nabla_\Gamma \cdot (m(\Phi_0)\partial_z M_0\boldsymbol{\nu})$$
$$+\partial_z(m(\Phi_0)\partial_z M_2 + m'(\Phi_0)\Phi_1\partial_z M_1) + \nabla_\Gamma \cdot (m(\Phi_0)\partial_z M_1\boldsymbol{\nu}) + \nabla_\Gamma \cdot (m(\Phi_0)\nabla_\Gamma M_0)\,.$$

Using $\partial_z M_0 = 0$ we obtain from (4.3) at order $\frac{1}{\varepsilon^2}$

$$0 = \partial_z(m(\Phi_0)\partial_z M_1).$$

Matching gives

$$m(\Phi_0)\partial_z M_1 \to 0 \quad \text{for} \quad z \to \pm\infty.$$

Hence $m(\Phi_0)\partial_z M_1 = 0$ and

$$M_1 = M_1(s, t).$$

At order $\frac{1}{\varepsilon}$ we obtain from (4.3), using $\partial_z M_1 = 0$ and $\partial_z M_0 = 0$,

$$-\mathcal{V}\partial_z\Phi_0 + (\mathbf{V}_0 \cdot \boldsymbol{\nu})\partial_z\Phi_0 = \partial_z(m(\Phi_0)\partial_z M_2) + \nabla_\Gamma \cdot (m(\Phi_0)\nabla_\Gamma M_0). \qquad (4.26)$$

Matching gives

$$m(\Phi_0)\partial_z M_2 \to 0 \quad \text{for} \quad z \to \pm\infty.$$

Integrating (4.26) gives

$$2(-\mathcal{V} + \mathbf{v}_0 \cdot \boldsymbol{\nu}) = \int_{-\infty}^{\infty} \nabla_\Gamma \cdot (m(\Phi_0)\nabla_\Gamma M_0)dz.$$

Since $m(\Phi_0)$ does not depend on s, we obtain $\nabla_\Gamma \cdot (m(\Phi_0)\nabla_\Gamma M_0) = m(\Phi_0)\Delta_\Gamma M_0$. Altogether we deduced

$$2(-\mathcal{V} + \mathbf{v}_0 \cdot \boldsymbol{\nu}) = \hat{m}\Delta_\Gamma \mu_0$$

where $\hat{m} = \int_{-\infty}^{\infty} m(\Phi_0)dz$.

Finally we deduce the flux balance for w at the interface in the limit $\varepsilon \to 0$. Equation (4.5) gives to order $\frac{1}{\varepsilon}$

$$-\mathcal{V}\partial_z W_0 + (\mathbf{V}_0 \cdot \boldsymbol{\nu})\partial_z W_0 = \partial_z(K(\Phi_0)W_0\partial_z(g''(W_0)W_1 + \beta'(\Phi_0)\Phi_1)). \qquad (4.27)$$

Matching gives

$$\partial_z(g''(W_0)W_1 + \beta'(\Phi_0)\Phi_1) \to \nabla(g'(w_0) + \beta(\pm 1)) \cdot \boldsymbol{\nu}$$

for $z \to \pm\infty$. Integrating (4.27) gives

$$(\mathcal{V} - \mathbf{v}_0 \cdot \boldsymbol{\nu})[w_0]_-^+ = -[Kw_0\nabla g'(w_0)]_-^+ \cdot \boldsymbol{\nu}.$$

In the case $g(w) = w\log w - w$ this identity reduces to

$$(\mathcal{V} - \mathbf{v}_0 \cdot \boldsymbol{\nu})[w_0]_-^+ = -[K\nabla w_0]_-^+ \cdot \boldsymbol{\nu}.$$

5 Free energy inequalities for the sharp interface limit

The sharp interface limit is now given as follows. We search for a smoothly evolving hypersurface Γ which for all $t \geq 0$ separates Ω into open sets $\Omega_-(t)$ and $\Omega_+(t)$ and we look for functions $\mathbf{v}, p, w$ which are all defined for $x \in \Omega$ and $t \geq 0$. In the cases I and III we seek in addition a chemical potential μ which in case I is defined on $\Omega \times (0, \infty)$ and for case III the potential μ is defined on the interface Γ only.

Assuming for g the form $g(w) = w(\log w - 1)$ we need to solve in all four cases the system

$$
\begin{aligned}
\rho_i(\partial_t \mathbf{v} + \operatorname{div}(\mathbf{v} \otimes \mathbf{v})) - \eta_i \Delta \mathbf{v} + \nabla p &= 0, \\
\operatorname{div} \mathbf{v} &= 0, \\
\partial_t w + \mathbf{v} \cdot \nabla w &= K_i \Delta w
\end{aligned}
$$

in the bulk regions Ω_- and Ω_+. In case I we in addition solve

$$
\Delta \mu = 0
$$

in the bulk. On the interface Γ we require

$$
\begin{aligned}
[\mathbf{v}]_-^+ &= 0, \\
\frac{w_2}{w_1} &= \exp(\beta_1 - \beta_2), \\
(\mathcal{V} - \mathbf{v} \cdot \boldsymbol{\nu})[w]_-^+ &= -[K \nabla w]_-^+ \cdot \boldsymbol{\nu}
\end{aligned}
$$

where $w_1 = w(x-)$ and $w_2 = w(x+)$. All other conditions depend on which of the cases I-IV we consider.

Case I ($m_\varepsilon(\varphi) = m_0$):

$$
\begin{aligned}
[\rho]_-^+ \mathbf{v}(\mathbf{v} \cdot \boldsymbol{\nu} - \mathcal{V}) - [2\eta D\mathbf{v}]_-^+ \boldsymbol{\nu} + [p]_-^+ \boldsymbol{\nu} &= \sigma \kappa \boldsymbol{\nu}, & (5.1) \\
2(\mathbf{v} \cdot \boldsymbol{\nu} - \mathcal{V}) &= m_0 [\nabla \mu]_-^+ \cdot \boldsymbol{\nu}, & (5.2) \\
2\mu &= \sigma \kappa - \tfrac{1}{2}|\mathbf{v}|^2 [\rho]_-^+ - [w]_-^+. & (5.3)
\end{aligned}
$$

Remarkable here is that the additional term $[\rho]_-^+ \mathbf{v}(\mathbf{v} \cdot \boldsymbol{\nu} - \mathcal{V})$ enters the stress balance at the interface. We also note that the non-standard term $\frac{1}{2}|\mathbf{v}|^2 [\rho]_-^+$ enters the Gibbs–Thomson law.

Cases II and IV ($\lim_{\varepsilon \to 0} m_\varepsilon(\phi) = 0$):

$$
\begin{aligned}
-[2\eta D\mathbf{v}]_-^+ \cdot \boldsymbol{\nu} + [p]_-^+ \boldsymbol{\nu} &= \sigma \kappa \boldsymbol{\nu}, \\
\mathcal{V} &= \mathbf{v} \cdot \boldsymbol{\nu},
\end{aligned}
$$

i.e., in this case we recover a standard free boundary problem for the Navier-Stokes system which in addition is coupled to the flow of a soluble species.

Case III $(m_\varepsilon(\varphi) = m_1(1 - \varphi^2)_+)$:
Beside (5.1) and (5.3) the identity

$$2(\mathbf{v} \cdot \boldsymbol{\nu} - \mathcal{V}) = \hat{m} \Delta_\Gamma \mu$$

has to hold. In this case the diffusion of the two components is limited to the interfacial region. In fact the well-known surface diffusion flow $\mathcal{V} = \Delta_\Gamma \kappa$, see [26, 6, 12, 13], is in the new model coupled to fluid flow.

In all cases we require $\mathbf{v} = 0$, $\nabla w \cdot \boldsymbol{\nu} = 0$ on $\partial\Omega$ and in case I we in addition require $\nabla \mu \cdot \boldsymbol{\nu} = 0$ on $\partial\Omega$. In order to derive a free energy inequality for the sharp interface limit we need the following transport identities, for a proof see [7].

Lemma 5.1 *(Transport identities). Let $\Gamma = (\Gamma(t))_{t\geq 0}$ with $\Gamma(t) \subset \Omega$, for all $t \geq 0$, be a smooth evolving hypersurface and let f be a quantity which is smooth for all $t \geq 0$ and $x \in \Omega \setminus \Gamma(t)$ and such that $[f]_-^+$ exists at Γ. Then it holds*

$$\frac{d}{dt} \int_{\Gamma(t)} 1 \, ds_x = - \int_{\Gamma(t)} \kappa \mathcal{V} \, ds_x = - \int_{\Gamma(t)} (\kappa \boldsymbol{\nu}) \cdot (\mathcal{V} \boldsymbol{\nu}) \, ds_x$$

and

$$\frac{d}{dt} \int_\Omega f dx = \int_\Omega \partial_t f dx - \int_{\Gamma(t)} [f]_-^+ \mathcal{V} \, ds_x \,.$$

We are now in a position to compute the dissipation rate and in conclusion derive a free energy inequality.

Theorem 5.2 *(Free energy inequality).*
A sufficiently smooth solution of the sharp interface problem with $\Gamma(t) \subset \Omega$, for all $t \geq 0$, fulfills

$$\frac{d}{dt} \left[\int_\Omega \left(\frac{\rho}{2} |\mathbf{v}|^2 + (g(w) + \beta w) \right) dx + \int_{\Gamma(t)} \sigma \, ds_x \right] = -\mathcal{D} \leq 0 \,,$$

provided the integrals are finite. Here $\rho = \rho_1, \rho_2$ and $\beta = \beta_1, \beta_2$ in the two phases. The quantity $\mathcal{D}$ is given as

$$\text{Case I} \qquad : \quad \mathcal{D} = \int_\Omega 2\eta |D\mathbf{v}|^2 dx + \int_\Omega K \tfrac{1}{w} |\nabla w|^2 dx + \int_\Omega m_0 |\nabla \mu|^2 dx \,,$$

$$\text{Case II and IV} \quad : \quad \mathcal{D} = \int_\Omega 2\eta |D\mathbf{v}|^2 dx + \int_\Omega K \tfrac{1}{w} |\nabla w|^2 dx \,,$$

$$\text{Case III} \qquad : \quad \mathcal{D} = \int_\Omega 2\eta |D\mathbf{v}|^2 dx + \int_\Omega K \tfrac{1}{w} |\nabla w|^2 dx + \int_{\Gamma(t)} \hat{m} |\nabla_\Gamma \mu|^2 ds_x \,.$$

Proof: We now give a proof for the cases I and III in detail and discuss the cases II and IV afterwards. For the kinetic energy we compute, using a transport identity,

$$
\frac{d}{dt} \int_\Omega \rho \frac{|\mathbf{v}|^2}{2} \, dx = \int_\Omega \rho \mathbf{v} \cdot \partial_t \mathbf{v} \, dx - \int_{\Gamma(t)} [\rho]_-^+ \frac{|\mathbf{v}|^2}{2} \mathcal{V} \, ds_x
$$

$$
= \int_\Omega \mathbf{v} \cdot (-\rho \operatorname{div}(\mathbf{v} \otimes \mathbf{v}) + 2\eta \operatorname{div} D\mathbf{v} - \nabla p) \, dx - \int_{\Gamma(t)} [\rho]_-^+ \frac{|\mathbf{v}|^2}{2} \mathcal{V} \, ds_x .
$$

Using $\operatorname{div} \mathbf{v} = 0$ we obtain $\operatorname{div}(\mathbf{v} \otimes \mathbf{v}) \cdot \mathbf{v} = \frac{1}{2} \nabla |\mathbf{v}|^2 \cdot \mathbf{v}$. Integration by parts on Ω_+ and Ω_- now gives

$$
\frac{d}{dt} \int_\Omega \rho \frac{|\mathbf{v}|^2}{2} \, dx = -\int_\Omega 2\eta |D\mathbf{v}|^2 \, dx + \int_{\Gamma(t)} \mathbf{v} \cdot (\tfrac{1}{2}[\rho]_-^+ |\mathbf{v}|^2 \boldsymbol{\nu} - [2\eta D\mathbf{v}]_-^+ \boldsymbol{\nu} + [p]_-^+ \boldsymbol{\nu}) \, ds_x
$$

$$
- \int_{\Gamma(t)} \tfrac{1}{2} [\rho]_-^+ |\mathbf{v}|^2 \mathcal{V} \, ds_x
$$

$$
= -\int_\Omega 2\eta |D\mathbf{v}|^2 \, dx + \int_{\Gamma(t)} (-\tfrac{1}{2} [\rho]_-^+ |\mathbf{v}|^2 (\mathbf{v} \cdot \boldsymbol{\nu} - \mathcal{V}) + \sigma \kappa \mathbf{v} \cdot \boldsymbol{\nu}) \, ds_x
$$

where we used the stress balance (5.1) and the fact that $\mathbf{v}$ is continuous.

The total free energy of the soluble species fulfills (using $g(w) = w \log w - w$)

$$
\frac{d}{dt} \int_\Omega (g(w) + \beta w) dx = \int_\Omega \partial_t w (\log w + \beta) \, dx - \int_{\Gamma(t)} [g(w) + \beta w]_-^+ \mathcal{V} \, ds_x .
$$

Since $\partial_t w + \mathbf{v} \cdot \nabla w = K \nabla \cdot (w \nabla \log w)$, we obtain

$$
\int_\Omega \partial_t w (\log w + \beta) \, dx = \int_\Omega (\log w + \beta)(-\mathbf{v} \cdot \nabla w + K \nabla \cdot (w \nabla \log w)) \, dx
$$

$$
= -\int_\Omega \mathbf{v} \cdot \nabla(g(w) + \beta w) \, dx - \int_\Omega K w |\nabla \log w|^2 \, dx
$$

$$
- \int_{\Gamma(t)} [(w \log w + \beta w) K \nabla \log w]_-^+ \cdot \boldsymbol{\nu} \, ds_x
$$

$$
= -\int_\Omega K w |\nabla \log w|^2 \, dx + \int_{\Gamma(t)} [g(w) + \beta w]_-^+ \mathbf{v} \cdot \boldsymbol{\nu} \, ds_x
$$

$$
- \int_{\Gamma(t)} [(\log w + \beta) K \nabla w]_-^+ \cdot \boldsymbol{\nu} \, ds_x
$$

$$
= -\int_\Omega K w |\nabla \log w|^2 \, dx + \int_{\Gamma(t)} [g(w) + \beta w]_-^+ \mathbf{v} \cdot \boldsymbol{\nu} \, ds_x
$$

$$
+ \int_{\Gamma(t)} (\log w + \beta)(\mathcal{V} - \mathbf{v} \cdot \boldsymbol{\nu})[w]_-^+ \, ds_x
$$

where we used $\operatorname{div} \mathbf{v} = 0$ and the fact that Henry's law implies the continuity of $\log w + \beta$. In addition we have

$$
\frac{d}{dt} \int_{\Gamma(t)} \sigma \, ds_x = -\int_{\Gamma(t)} \sigma \kappa \mathcal{V} \, ds_x .
$$

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Altogether we obtain using the generalized Gibbs–Thomson law (5.3) and the fact that $g(w) + \beta w - (\log w + \beta)w = -w$

$$\frac{d}{dt}\left(\int_\Omega \left(\rho\frac{|\mathbf{v}|^2}{2} + g(w) + \beta w\right) dx + \int_{\Gamma(t)} \sigma\, ds_x\right) \tag{5.4}$$

$$= -\int_\Omega 2\eta|D\mathbf{v}|^2\, dx - \int_\Omega K\frac{1}{w}|\nabla w|^2\, dx$$

$$+ \int_{\Gamma(t)} (\mathbf{v}\cdot\boldsymbol{\nu} - \mathcal{V})(-\tfrac{1}{2}[\rho]_-^+|\mathbf{v}|^2 + \sigma\kappa - [w]_-^+)\, ds_x$$

$$= -\int_\Omega 2\eta|D\mathbf{v}|^2\, dx - \int_\Omega K\frac{1}{w}|\nabla w|^2\, dx + \int_{\Gamma(t)} (\mathbf{v}\cdot\boldsymbol{\nu} - \mathcal{V})2\mu\, ds_x\,.$$

In case I we obtain by integration by parts using (5.2) and $\Delta\mu = 0$ in the bulk

$$\int_{\Gamma(t)} 2(\mathbf{v}\cdot\boldsymbol{\nu} - \mathcal{V})\mu\, ds_x = \int_{\Gamma(t)} m_0\mu[\nabla\mu]_-^+\cdot\boldsymbol{\nu}\, ds_x \tag{5.5}$$

$$= -\int_\Omega \nabla\cdot(\mu m_0\nabla\mu)\, dx = -\int_\Omega m_0|\nabla\mu|^2\, dx\,.$$

In case III we obtain using integration by parts on manifolds without boundary

$$\int_{\Gamma(t)} 2(\mathbf{v}\cdot\boldsymbol{\nu} - \mathcal{V})\mu\, ds_x = \int_{\Gamma(t)} \hat{m}(\Delta_\Gamma\mu)\mu\, ds_x = -\int_{\Gamma(t)} \hat{m}|\nabla_\Gamma\mu|^2\, ds_x. \tag{5.6}$$

Combining (5.4)-(5.6) gives the result in the cases I and III. In the cases II and IV we have $\mathcal{V} = \mathbf{v}\cdot\boldsymbol{\nu}$ and the calculations simplify. In particular we do not need to treat the term $\int_{\Gamma(t)}(\mathbf{v}\cdot\boldsymbol{\nu} - \mathcal{V})2\mu\, ds_x$ and diffusion plays no role for the fluid flow. ∎

Appendix

We use the notation of Section 4.3 and prove the identities (4.10), 4.11) and (4.12). Let $(s_1, \ldots, s_{d-1}) \in U$ and $G_x^\varepsilon(s, z) = \boldsymbol{\gamma}(s) + \varepsilon z\boldsymbol{\nu}(s)$, where here and in what follows we omit the t-dependence. Then

$$\partial_{s_1}\boldsymbol{\gamma} + \varepsilon z\partial_{s_1}\boldsymbol{\nu}, \ldots, \partial_{s_{d-1}}\boldsymbol{\gamma} + \varepsilon z\partial_{s_{d-1}}\boldsymbol{\nu},\ \varepsilon\boldsymbol{\nu}$$

is a basis of $\mathbb{R}^d$ locally around Γ. We define the metric tensor in the new coordinates as follows

$$\begin{aligned}
g_{ij} &= (\partial_{s_i}\boldsymbol{\gamma} + \varepsilon z\partial_{s_i}\boldsymbol{\nu})\cdot(\partial_{s_j}\boldsymbol{\gamma} + \varepsilon z\partial_{s_j}\boldsymbol{\nu}) \quad i,j = 1,\ldots,d-1\,,\\
g_{id} &= g_{di} = (\partial_{s_i}\boldsymbol{\gamma} + \varepsilon z\partial_{s_i}\boldsymbol{\nu})\cdot\varepsilon\boldsymbol{\nu} = 0 \quad i = 1,\ldots,d-1\,,\\
g_{dd} &= \varepsilon\boldsymbol{\nu}\cdot\varepsilon\boldsymbol{\nu} = \varepsilon^2
\end{aligned}$$

where we used that $\partial_{s_i}\boldsymbol{\nu}\cdot\boldsymbol{\nu} = \frac{1}{2}\partial_{s_i}|\boldsymbol{\nu}|^2 = 0$. We set

$$\mathcal{G}_{\varepsilon z} = (g_{ij})_{i,j=1,\ldots,d}, \ \hat{\mathcal{G}}_{\varepsilon z} = (g_{ij})_{i,j=1,\ldots,d-1}, \ (\mathcal{G}_{\varepsilon z})^{-1} = (g^{ij})_{i,j=1,\ldots,d}, (\hat{\mathcal{G}}_{\varepsilon z})^{-1} = (g^{ij})_{i,j=1,\ldots,d-1}$$

and hence

$$\mathcal{G}_{\varepsilon z} = \begin{pmatrix} & & 0 \\ \hat{\mathcal{G}}_{\varepsilon z} & & \vdots \\ & & 0 \\ 0\cdots 0 & \varepsilon^2 \end{pmatrix}, \ (\mathcal{G}_{\varepsilon z})^{-1} = \begin{pmatrix} & & 0 \\ (\hat{\mathcal{G}}_{\varepsilon z})^{-1} & & \vdots \\ & & 0 \\ 0\cdots 0 & \varepsilon^{-2} \end{pmatrix}.$$

Denoting by s_d the z-variable we have for a scalar function $b(t,x) = \hat{b}(t,s(t,x),z(t,x))$

$$\begin{aligned} \nabla_x b &= \sum_{i,j=1}^{d} g^{ij}\partial_{s_i}\hat{b}\,\partial_{s_j}G_x^\varepsilon = \sum_{i,j=1}^{d-1} g^{ij}\partial_{s_i}\hat{b}\,\partial_{s_j}G_x^\varepsilon + \tfrac{1}{\varepsilon^2}\partial_z\hat{b}\,\partial_z G_x^\varepsilon \\ &= \nabla_{\Gamma_{\varepsilon z}}\hat{b} + \tfrac{1}{\varepsilon}\partial_z\hat{b}\,\boldsymbol{\nu} \end{aligned}$$

where we used the fact that $g_{id} = 0$ for $i = 1,\ldots,d-1$. Here $\nabla_{\Gamma_{\varepsilon z}}\hat{b}$ is the tangential gradient $\nabla_{\Gamma_{\varepsilon z}}b_{|\Gamma_{\varepsilon z}}$ on $\Gamma_{\varepsilon z} := \{\boldsymbol{\gamma}(s) + \varepsilon z\boldsymbol{\nu}(s) \mid s \in U\}$. In addition we compute for a vector quantity $\mathbf{j}(t,x) = \hat{\mathbf{j}}(t,s(t,x),z(t,x))$

$$\begin{aligned} \nabla_x \cdot \mathbf{j} &= \sum_{i,j=1}^{d} g^{ij}\partial_{s_i}\hat{\mathbf{j}}\cdot\partial_{s_j}G_x^\varepsilon = \sum_{i,j=1}^{d-1} g^{ij}\partial_{s_i}\hat{\mathbf{j}}\cdot\partial_{s_j}G_x^\varepsilon + \tfrac{1}{\varepsilon^2}\partial_z\hat{\mathbf{j}}\cdot\varepsilon\boldsymbol{\nu} \quad (5.7) \\ &= \nabla_{\Gamma_{\varepsilon z}}\cdot\hat{\mathbf{j}} + \tfrac{1}{\varepsilon}\partial_z\hat{\mathbf{j}}\cdot\boldsymbol{\nu}, \end{aligned}$$

where $\nabla_{\Gamma_{\varepsilon z}}\cdot\hat{\mathbf{j}}$ is the divergence on $\Gamma_{\varepsilon z}$. We remark that $\nabla_{\Gamma_{\varepsilon z}}\hat{b}\cdot\boldsymbol{\nu} = 0$, as $\boldsymbol{\nu}$ is normal to $\Gamma_{\varepsilon z}$. We hence obtain

$$\partial_z(\nabla_{\Gamma_{\varepsilon z}}\hat{b}\cdot\boldsymbol{\nu}) = 0$$

and

$$\partial_z(\nabla_{\Gamma_{\varepsilon z}}\hat{b})\cdot\boldsymbol{\nu} + \nabla_{\Gamma_{\varepsilon z}}b\cdot\partial_z\boldsymbol{\nu} = 0.$$

Since $\partial_z\boldsymbol{\nu} = 0$, we get

$$(\partial_z\nabla_{\Gamma_{\varepsilon z}}\hat{b})\cdot\boldsymbol{\nu} = 0.$$

We now compute

$$\begin{aligned} \Delta_x b &= \nabla_x\cdot(\nabla_x b) = \nabla_x\cdot(\nabla_{\Gamma_{\varepsilon z}}\hat{b} + \tfrac{1}{\varepsilon}\partial_z\hat{b}\,\boldsymbol{\nu}) \\ &= \nabla_{\Gamma_{\varepsilon z}}\cdot(\nabla_{\Gamma_{\varepsilon z}}\hat{b}) + \tfrac{1}{\varepsilon}(\nabla_{\Gamma_{\varepsilon z}}\partial_z\hat{b})\cdot\boldsymbol{\nu} \\ &\quad + \tfrac{1}{\varepsilon}\partial_z\hat{b}\nabla_{\Gamma_{\varepsilon z}}\cdot\boldsymbol{\nu} + \tfrac{1}{\varepsilon}(\partial_z\nabla_{\Gamma_{\varepsilon z}}\hat{b})\cdot\boldsymbol{\nu} + \tfrac{1}{\varepsilon^2}\partial_{zz}\hat{b}\cdot\boldsymbol{\nu} + \tfrac{1}{\varepsilon^2}\partial_z\hat{b}\,\partial_z\boldsymbol{\nu}\cdot\boldsymbol{\nu}. \end{aligned}$$

Because of $(\nabla_{\Gamma_{\varepsilon z}}\partial_z\hat{b})\cdot\boldsymbol{\nu} = 0$, $(\partial_z\nabla_{\Gamma_{\varepsilon z}}\hat{b})\cdot\boldsymbol{\nu} = 0$, $\boldsymbol{\nu} = \nabla_x d$, (5.7) and $\partial_z\boldsymbol{\nu} = 0$, we obtain

$$\Delta_x b = \Delta_{\Gamma_{\varepsilon z}}\hat{b} + \tfrac{1}{\varepsilon}(\Delta_x d)\partial_z\hat{b} + \tfrac{1}{\varepsilon^2}\partial_{zz}\hat{b}.$$

Introducing $g_{\varepsilon z} = \det \mathcal{G}_{\varepsilon z}$ we get

$$\Delta_{\Gamma_{\varepsilon z}}\hat{b} = \frac{1}{\sqrt{g_{\varepsilon z}}} \sum_{i,j=1}^{d-1} \partial_{s_i}(\sqrt{g_{\varepsilon z}}g^{ij}\partial_{s_j}\hat{b}) \,.$$

Since

$$g_{ij} = \partial_{s_i}\boldsymbol{\gamma} \cdot \partial_{s_j}\boldsymbol{\gamma} + \text{ h.o.t.}, \ i,j = 1,\ldots,d-1,$$

we derive

$$\begin{aligned}
\nabla_{\Gamma_{\varepsilon z}}\hat{b}(s,z) &= \nabla_\Gamma\hat{b}(s,z) + \text{ h.o.t.}, \\
\nabla_{\Gamma_{\varepsilon z}} \cdot \hat{\mathbf{j}}(s,z) &= \nabla_\Gamma \cdot \hat{\mathbf{j}}(s,z) + \text{ h.o.t.}, \\
\Delta_{\Gamma_{\varepsilon z}}\hat{b}(s,z) &= \Delta_\Gamma\hat{b}(s,z) + \text{ h.o.t.}
\end{aligned}$$

where $\nabla_\Gamma, \nabla_\Gamma\cdot$ and Δ_Γ are computed on $\Gamma_{\varepsilon z}$ with the metric tensor $\mathcal{G}_0$. From Gilbarg and Trudinger [19] (Lemma 14.17) we get (denoting by κ_i the principal curvatures)

$$\begin{aligned}
\Delta_x d &= \sum_{i=1}^{d-1}\frac{-\kappa_i}{1-\kappa_i d} = \sum_{i=1}^{d-1}\frac{-\kappa_i}{1-\varepsilon\kappa_i z} = -\sum_{i=1}^{d-1}\kappa_i - \sum_{i=1}^{d-1}\varepsilon\kappa_i^2 z + \text{ h.o.t.} \\
&= -\kappa - \varepsilon z|\mathcal{S}|^2 + \text{ h.o.t.},
\end{aligned}$$

where κ is the mean curvature and $|\mathcal{S}|$ is the spectral norm of the Weingarten map $\mathcal{S}$.

Hence we obtain

$$\Delta_x b = \Delta_\Gamma\hat{b} - \tfrac{1}{\varepsilon}(\kappa + \varepsilon z|\mathcal{S}|^2)\partial_z\hat{b} + \tfrac{1}{\varepsilon^2}\partial_{zz}\hat{b} + \text{ h.o.t.}.$$

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